Monomolybdononavanadate and *cis*- and *trans*-Dimolybdo-octavanadate†

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Molybdenum(VI) is shown to replace 'capping' vanadium(V) in the decavanadate structure, once to yield monomolybdononavanadate $[MoV_9O_{28}]^{5-}$, or twice to yield dimolybdo-octavanadates $[Mo_2V_8O_{28}]^{4-}$. By potentiometry and ^{51}V, ^{17}O, and ^{95}Mo n.m.r. spectroscopy, including $^{51}V-^{51}V$ correlation spectroscopy, the speciation and unequivocal assignment of shifts and structures have been established. The ion $[MoV_9O_{28}]^{5-}$ protonates primarily at the bridging oxygens furthest from Mo, with $pK_a = 2.8$ (0.6 mol dm^{-3} NaCl), $[Mo_2V_8O_{28}]^{4-}$ does not protonate, and exists in two forms, *cis* and *trans*, present in the ratio 9:11. No other isomer was found. The replacement of V by Mo in decavanadate is shown by ^{17}O labelling to involve a complete reformation of the polyanion's structure.

Although there has been substantial study of both isopolymolybdates(VI)[1–3] and of isopolyvanadates(V)[1,4–7] relatively little is known about molybdovanadates. A study was therefore initiated in Umeå about ten years ago. The aim was to establish the speciation in the aqueous system and to determine the structures of the main species, by using an e.m.f. titration technique. The e.m.f. effects were, however, rather small, due to the fact that the molybdovanadate heteropolyanion species 'consume' protons much the same as the species formed in the isopolymolybdate and isopolyvanadate subsystems. Potentiometry was thus found not to be sufficient for establishing the speciation. To acquire complementary information, crystallisation experiments were performed. A variety of molybdovanadate phases were obtained and the crystal structures of a few molybdenum-rich molybdovanadate polyanions have been reported, α-$[Mo_6V_2O_{26}]^{6-}$,[8] β-$[Mo_6V_2O_{26}]^{6-}$,[9] $[Mo_8V_5O_{40}]^{7-}$,[10] $[HMo_9V_3O_{38}]^{6-}$,[11] together with $[Mo_4V_8O_{36}]^{8-}$.[12] However, none of these structures correlates with any of the major species observed in solution.

As combined e.m.f.–n.m.r. measurements had proved to be very valuable in solving the speciation in the isopolyvanadate system,[4–7] such a combined study was started a few years ago on the molybdovanadate system. Vanadium-51 n.m.r. spectra, which were originally recorded on a 250-MHz spectrometer, revealed that the system was extremely complex. Moreover, many of the n.m.r. peaks often severely overlapped. To obtain quantitative peak integral data, a higher field had to be used. Most recent spectra have been recorded on a 400-MHz apparatus.

During the course of the present investigation Maksimovskaya and Chumachenko[13] have published a solution study. On the basis of ^{51}V n.m.r. chemical shifts and integrals they propose the existence of a monomolybdononavanadate $[MoV_9O_{28}]^{5-}$ having the well known decavanadate structure[14] but with Mo substituted for V at a 'capping'[7] position. Also, from the ^{51}V chemical shift alone, these authors propose two molybdenum-rich species, $[Mo_4V_2O_{19}]^{4-}$ and $[Mo_5VO_{19}]^{3-}$, by analogy with known tungstovanadates.[15] The authors also note the presence of other species, as yet uncharacterised.

Our present study shows that the molybdovanadate system is indeed complex, particularly in the molybdenum-rich region. However, the vanadium-rich region contains only three species in significant proportion. Each is isostructural with decavanadate. We confirm Maksimovskaya and Chumachenko's proposal that a single molybdenum substitution takes place at a 'capping' vanaduium site, and we also show that a second such substitution can take place at two of the three remaining capping sites. The structures are confirmed in each case by means of ^{17}O n.m.r. spectroscopy, and the vanadium resonances are assigned by two-dimensional homonuclear correlation spectroscopy (COSY).[16] The presence of further, molybdenum-rich species is evident in some of the figures; it is our intention to analyse these subsequently.

Experimental

N.M.R. Measurements.—^{51}V, ^{17}O, and ^{95}Mo n.m.r. spectra were obtained on a Bruker WH400 spectrometer at 105.2, 54.2, and 26.1 MHz respectively. The measurements were conducted at room temperature and at 99 °C, shifts being reported only at the lower temperature. No effects of chemical exchange were noted in the species reported here. One-dimensional ^{51}V n.m.r. spectra were typically recorded with 4 000 transients and at a concentration of 10—100 mmol dm^{-3} in 0.6 mol dm^{-3} Na(Cl) medium; medium effects were in fact small. Two-dimensional $^{51}V-^{51}V$ COSY spectra were obtained at 99 °C to minimise linewidths, and were processed with both sinebell windows, for maximum resolution, and also Gaussian windows when it was necessary to reduce the suppression of broader resonances. In general, slightly better results were obtained with COSY-90 rather than COSY-45. The ^{17}O and ^{95}Mo n.m.r. spectra were obtained at 1—2 mol dm^{-3}, the latter at 99 °C only to minimise linewidth. At higher temperatures it was partially possible to resolve ^{51}V couplings in the ^{17}O spectra, and their presence was a useful aid to assignment. Because the ^{17}O linewidths were fairly small, with no exchange broadening, it was possible to obtain reliable integrals ($\pm 15\%$) from many of the spectra, and these were valuable for assignment, especially when peaks overlapped. Variations of temperature, pH, and concentration were also employed to resolve overlaps. The ^{51}V integrals at 99 °C were mostly found to be reliable within $\pm 10\%$, although

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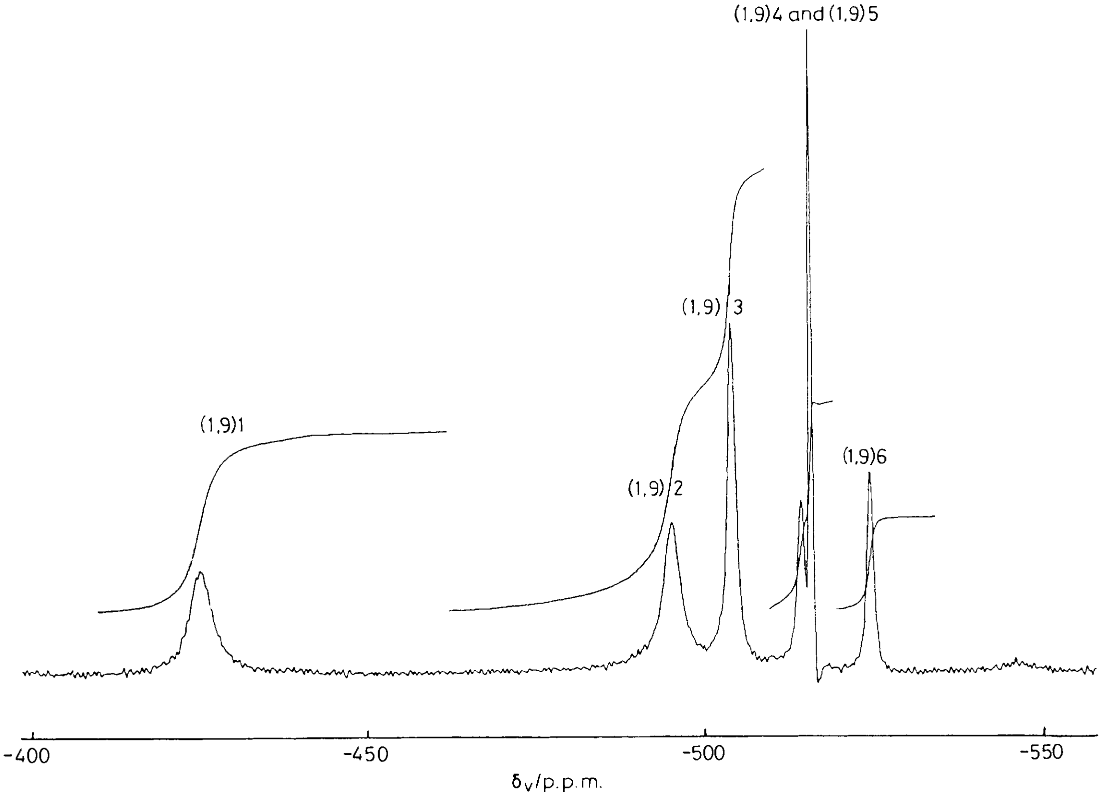

Figure 1. Vanadium-51 n.m.r. spectrum, pH 5.0, 45 mmol dm^{-3} in V and 5 mmol dm^{-3} in Mo, 294 K, from which has been subtracted a spectrum of decavanadate at the same pH, so as to show only the six peaks from $[MoV_9O_{28}]^{5-}$

some problems of baseline correction were found near to the largest and most crowded peak regions. These integrals exclude any other vanadium-rich species present as more than 5% of total metal, excepting $[VO_2]^+$ and known isopolyvanadates at pH extremes.

Chemicals and analyses were the same as described in ref. 5.

Notations.—The equilibria studied are written with H^+, $[MoO_4]^{2-}$, and $[HVO_4]^{2-}$ as components and thus the complexes are formed according to $pH^+ + q[MoO_4]^{2-} + r[HVO_4]^{2-} \rightleftharpoons (H^+)_p(MoO_4^{2-})_q(HVO_4^{2-})_r$. Equilibrium constants are denoted $\beta_{p,q,r}$. Complexes are, for brevity, often given the notation (p, q, r) or (q, r) for a homonuclear series.

E.m.f. Measurements.—The measurements were carried out as a series of potentiometric titrations in a 0.6 mol dm^{-3} Na(Cl) medium at 25 °C. The glass electrodes used were of the general purpose type, Ingold 201-NS. The free hydrogen ion concentration (in mol dm^{-3}) was calculated from the measured e.m.f. (E/mV) using equation (1) where the last term is the liquid

$$E = E_0 + 59.157 \log[H^+] - 76[H^+] \qquad (1)$$

junction potential. The constant E_0 was determined separately in solutions with known $[H^+]$ before and after each titration.

The potentiometric data cover the range $1.5 \leqslant -\log[H^+] \leqslant 7$. From now on $-\log[H^+]$ will be written pH. The vanadium concentration was mostly kept below 20 mmol dm^{-3}. Only results for the vanadium-rich species will be presented here.

When measuring the pH in separately prepared (sometimes highly) concentrated n.m.r. solutions a combination electrode (Copenhagen) was used and calibrated against buffer solutions. Such data have not been included in the e.m.f. calculations.

The titrations were performed at constant total concentrations of Mo and V by varying the pH in both directions and also at constant pH by varying the Mo:V ratio. These data were self-consistent. Equilibria are attained fairly rapidly except when decavanadate species are decomposed, where up to 24 h are needed to obtain stable e.m.f. values.

Results and Discussion

One-dimensional ^{51}V *N.M.R. Spectra.*—Figure 1 shows a ^{51}V n.m.r. spectrum of a solution 0.045 mol dm^{-3} in V and 0.005 mol dm^{-3} in Mo, at pH 5.0 and room temperature, from which has been subtracted a spectrum of decavanadate [Figure 2(*a*)] at the same pH, ionic medium, and temperature. Under these conditions it was possible to achieve a fairly good subtraction, and thus to demonstrate the (left to right) 2:2:2:1:1:1 peak area ratio for the single species with the lowest Mo:V ratio. These areas can only arise from Mo substituting for a capping V, as in Figure 2(*b*).

Unfortunately, such subtraction spectra were of limited use because of the marked dependence of many peak positions upon pH, as shown in Figure 3. However, the same pH dependence is useful in showing that several peaks show a common pK_a, and hence almost certainly belong to one species. In Figure 3, decavanadate peaks[17] and peaks arising from a putative (4,5) species (see below) are omitted for clarity. The curves labelled (4,2) and (5,1) correspond to the data and formulae proposed by Maksimovskaya and Chumachenko.[13] Peaks assigned to $[MoV_9O_{28}]^{5-}$ and its protonated form are labelled (1,9)*n*, where *n* increases with decreasing δ_V. Similarly, peaks from $[Mo_2V_8O_{28}]^{4-}$ are labelled as (2,8)*n*.

Table 1 supports these assignments, and the retention of a decavanadate structure [Figure 2(*a*)], because peak (1,9)1 is very close in shift to (0,10)1, peak (1,9)2 close to (0,10)2, and

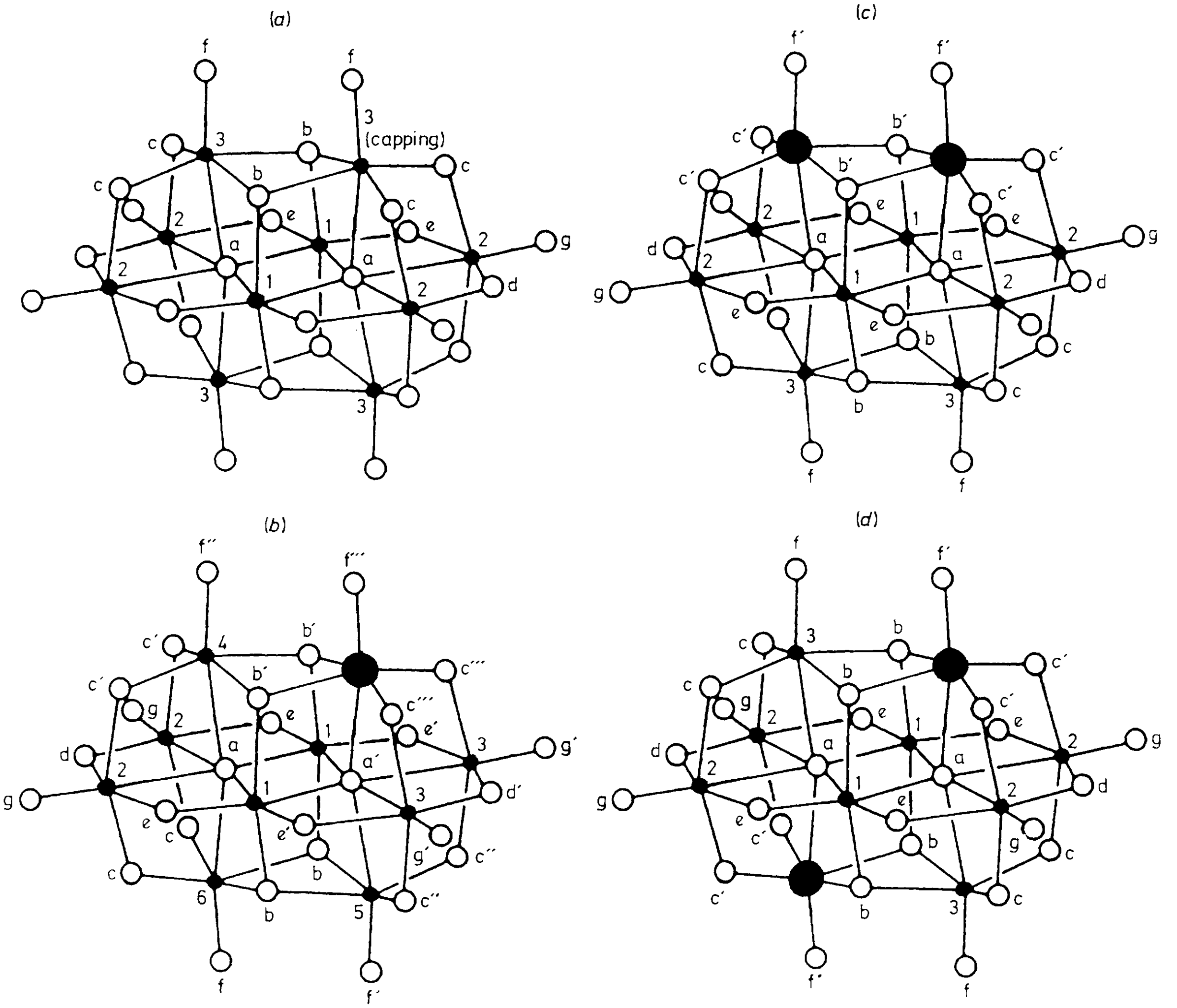

Figure 2. Proposed structures and labelling for (*a*) $[V_{10}O_{28}]^{6-}$,[18] (*b*) $[MoV_9O_{28}]^{5-}$, (*c*) *cis*-$[Mo_2V_8O_{28}]^{4-}$, and (*d*) *trans*-$[Mo_2V_8O_{28}]^{4-}$

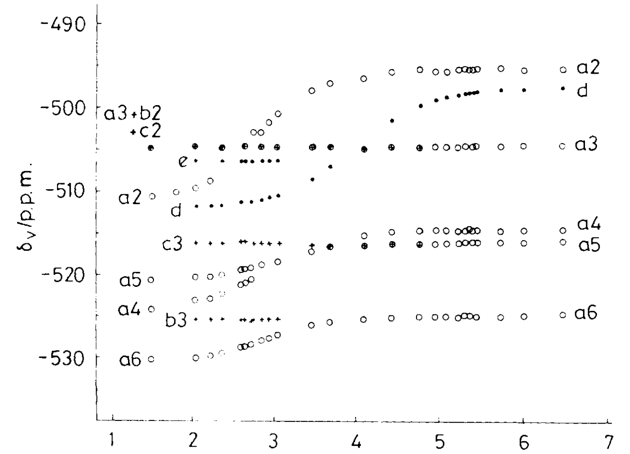

Figure 3. Dependence of ^{51}V n.m.r. resonances on pH, omitting high-frequency peaks and resonances from decavanadate and a possible (4,5) species, 294 K, 80 mmol dm^{-3} in V, 20 mmol dm^{-3} in Mo. Species: a = $[MoV_9O_{28}]^{5-}$ and $[HMoV_9O_{28}]^{4-}$; b = *cis*-$[Mo_2V_8O_{28}]^{4-}$; c = *trans*-$[Mo_2V_8O_{28}]^{4-}$; d = *cis*-$[Mo_4V_2O_{19}]^{4-}$ and *cis*-$[HMo_4V_2O_{19}]^{3-}$; e = $[Mo_5VO_{19}]^{3-}$; a3, for example, refers to peak 3 of species a

peaks (1,9)4 and (1,9)5 close to (0,10)3, in the unprotonated state. The other peaks, however, have been shifted by molybdenum substitution by up to 10 p.p.m. to lower frequency, presumably because of structural distortions created by molybdenum.

Two-dimensional ^{51}V–^{51}V *N.M.R. Spectra.*—All these resonances may be unambiguously assigned using two-dimensional ^{51}V–^{51}V COSY. This technique has previously been applied to decavanadate by Domaille,[16] but not to any previously unassigned resonances. Figure 4 shows the two-dimensional spectrum of a solution 0.05 mol dm^{-3} in both V and Mo, at pH 5.72. Under these conditions the dominant species are $[MoV_9O_{28}]^{5-}$ and a second species [probably (4,5)] whose structure will be discussed in a later paper. Couplings are revealed between peaks (1,9)2—4 and (1,9)3—5, as well as between some of the '(4,5)' peaks. Under slightly different conditions peaks can also be found connecting (1,9)1 with both (1,9)2 and (1,9)3. The only two-bond VOV couplings not revealed are 1—4, 1—5, and 1—6 using the assignment shown in Figure 2(*b*).

The COSY spectra also serve to elucidate the remaining resonances, all of which have shifts independent of pH, and many of which are obscured by overlaps. Figure 5 shows the COSY spectrum of a pH 1.99 solution 0.05 mol dm^{-3} in both V and Mo. The data have been processed using Gaussian

Table 1. Vanadium-51 n.m.r. chemical shifts (p.p.m.) at 294 K

$[V_{10}O_{28}]^{6-}$ [a]		$[MoV_9O_{28}]^{5-}$		$[HMoV_9O_{28}]^{4-}$ [b]	*trans*-$[Mo_2V_8O_{28}]^{4-}$		*cis*-$[Mo_2V_8O_{28}]^{4-}$	
Peak	δ_V [c]	Peak	δ_V [c]	δ_V	Peak	δ_V [c]	Peak	δ_V [c]
(0,10)1	−425(2) [d]	(1,9)1	−425(2)	−426	*trans*-(2,8)1	−427(2)	*cis*-(2,8)1	−424(2)
(0,10)2	−498(4)	(1,9)2	−495.5(2)	−510.6	*e*		*e*	
e		(1,9)3	−505(2)	−505	*trans*-(2,8)2	−505(4)	*cis*-(2,8)2	−505(4)
(0,10)3	−515(4)	(1,9)4	−514.9(1)	−524.2	*e*		*e*	
		(1,9)5	−516.2(1)	−520.7	*trans*-(2,8)3	−516.2(2)	*e*	
		(1,9)6	−525.3(1)	−530.4	*e*		*cis*-(2,8)3	−525.5(2)

[a] From ref. 17. [b] Estimated composition from pH curve. [c] Relative peak area in parentheses for compound in question. [d] Figures without decimal places are less accurate, *e.g.* due to overlap. [e] Not applicable.

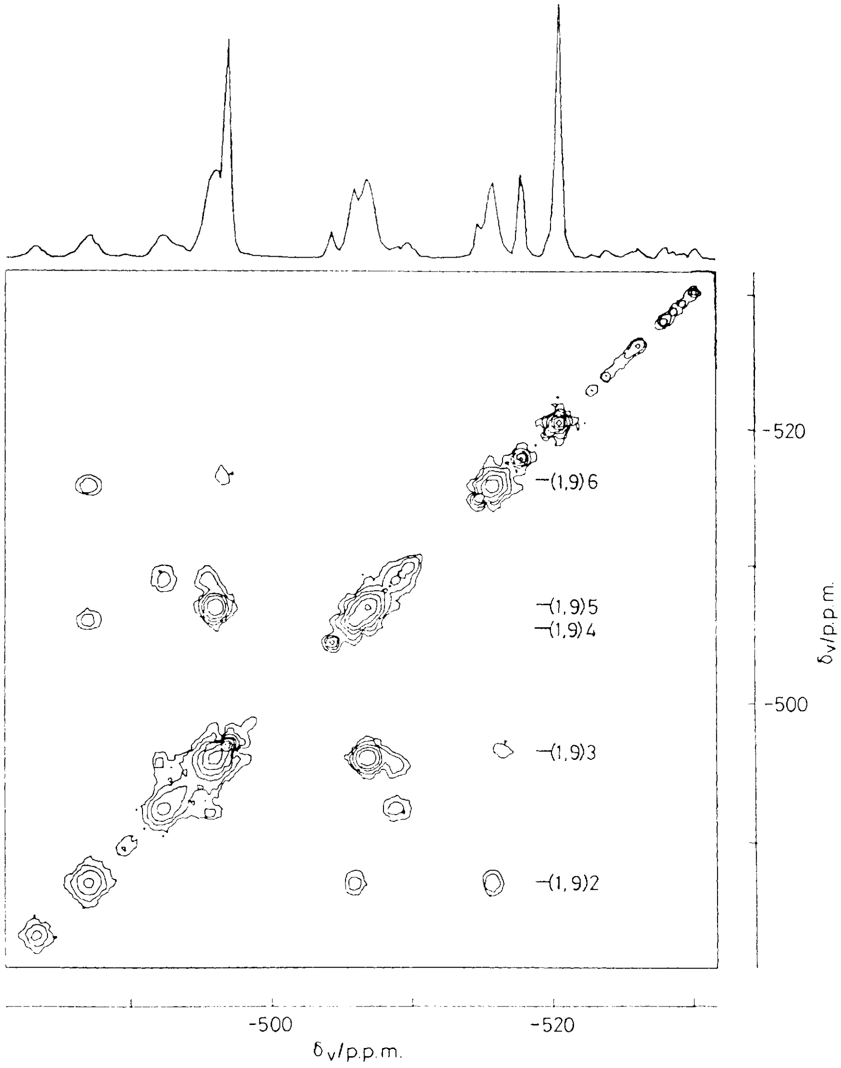

Figure 4. Low-frequency region of the ^{51}V–^{51}V COSY-90 spectrum, 50 mmol dm^{-3} in both V and Mo, pH 5.72, 99 °C with sinebell windows, showing the presence of couplings in $[MoV_9O_{28}]^{5-}$, and a further species

windows, which reduces resolution but enhances weak off-diagonal resonances, and here reveals the 1–2 and 2–3 couplings for two distinct further species. It also reveals a slight shift separation of the *cis*- and *trans*-(2,8)2 resonances, which could not be resolved in any one-dimensional spectrum.

The two new species are present in constant and nearly equal proportion under almost all conditions of temperature, concentration, and pH. Our best estimate is a *cis*:*trans* ratio (see below) of 9:11. The stoicheiometry of their formation, their spectra, and the potentiometric study described below show them to be *cis*- and *trans*-$[Mo_2V_8O_{28}]^{4-}$, with structures as shown in Figures 2(*c*) and (*d*); *cis* and *trans* here refer to the mutual relationship of 'capping' vanadiums, by analogy with ring protons. No other isomers can give the required 2:4:2 ratio of vanadium peak areas. The *trans* isomer is distinguishable from the *cis* by the ^{51}V chemical shift of its 3 resonance, which is

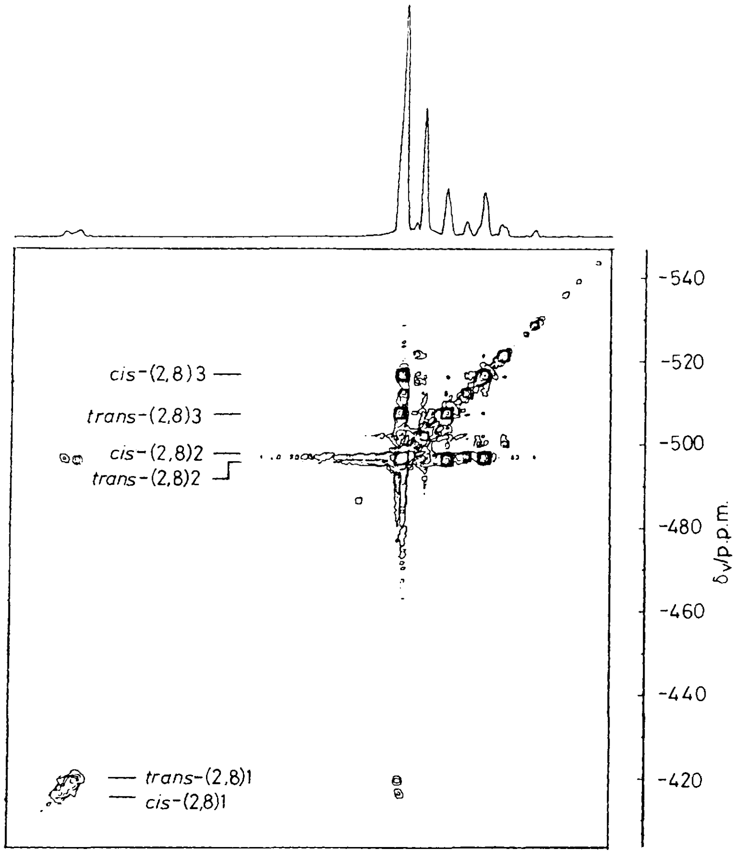

Figure 5. Full $^{51}V-^{51}V$ COSY-90 spectrum, 50 mmol dm^{-3} in both V and Mo, pH 1.99, with Gaussian windows to reveal and distinguish couplings to both the *cis*- and *trans*-(2,8)1 resonances

Table 2. Oxygen-17 n.m.r. chemical shifts (p.p.m.) at 294 K

Peak[a]	$[V_{10}O_{28}]^{6-}$[b]	$[MoV_9O_{28}]^{5-}$	$[HMoV_9O_{28}]^{4-}$[c]	*cis*-$[Mo_2V_8O_{28}]^{4-}$	*trans*-$[Mo_2V_8O_{28}]^{4-}$
a	55[d]	27.6	41.4	77.2	47.7
a′	n.a.	80.2	74.7	n.a.	n.a.
b′	n.a.	337.2	343.6	279.4	n.a.
b	420	438.7	410.1	446.7	355.1
c‴	n.a.	604.4	614.2	n.a.	n.a.
c′	n.a.	786	720	622	622
c	765	786	720	726	845
c″	n.a.	825	835.7	n.a.	n.a.
d	785	806	846.3	832	832
d′	n.a.	806	835.7	n.a.	n.a.
e	895	896.8	917.9	909.2	935
e′	n.a.	930.1	936	n.a.	n.a.
f‴	n.a.	881.4	896.1	n.a	n.a.
f	1 125	1 143	1 187	1 165	1 198
f′	n.a.	1 143	1 187	922.2	916
f″	n.a.	1 180	1 200	n.a.	n.a.
g	1 142	1 170.8	1 200	1 207	1 220
g′	n.a.	1 191	1 206.7	n.a.	n.a.
$\Sigma\delta_O$	22 128	22 002	22 077	21 310	21 934

n.a. = Not applicable because of higher symmetry. [a] Using labelling scheme of ref. 18 with added primes to indicate increasing proximity to Mo. [b] For comparison, from ref. 7. [c] Approximately monoprotonated, but precise state not definable. [d] δ_O (solvent water) = 0. Values without decimal places are less precise, *e.g.* due to overlap.

close to (1,9)6. The 10 p.p.m. shift of *cis* (2,8)3 to lower frequency must arise mainly from the vanadium's *trans* relationship to Mo, as with (1,9)6.

We have found no evidence for any $[Mo_3V_7O_{28}]^{3-}$ species, or for any *gem* (2,8).

Oxygen-17 *Resonances*.—The structures proposed in Figure 2 receive final confirmation from ^{17}O n.m.r. spectroscopy. A portion of a typical spectrum is shown in Figure 6, and chemical shifts are listed in Table 2. The peaks can be mostly assigned by area and by analogy with the known assignment of deca-

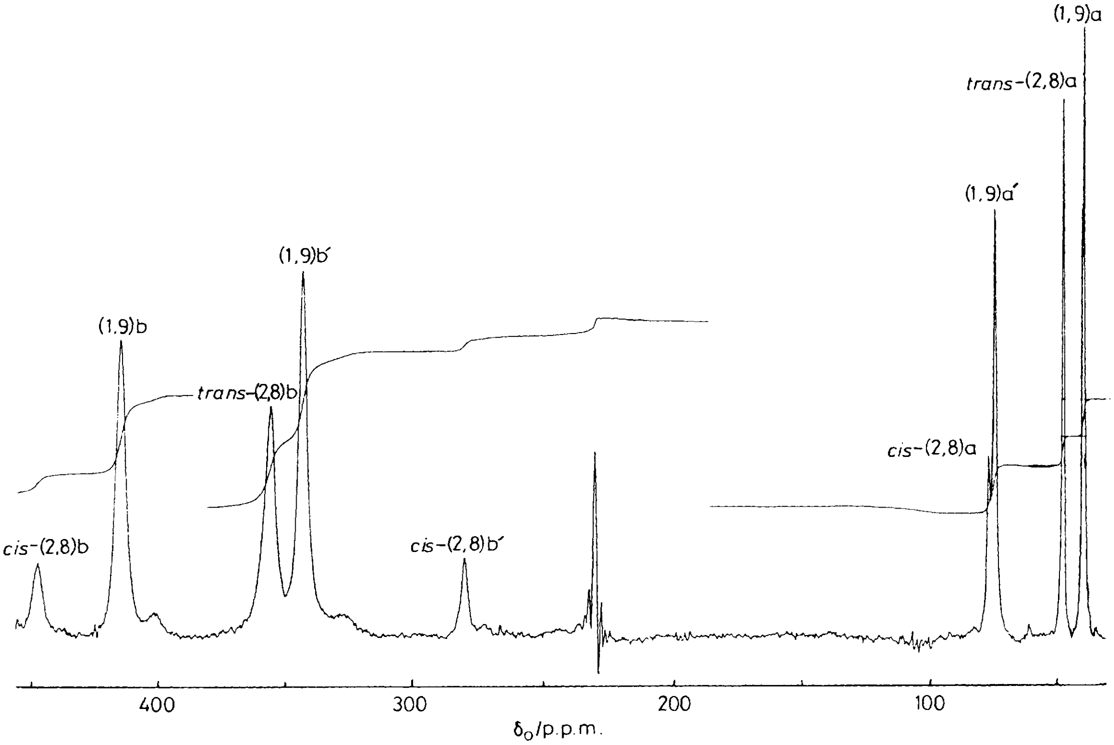

Figure 6. Partial ^{17}O n.m.r. spectrum of a solution *ca.* 1 mol dm^{-3} in V, 0.4 mol dm^{-3} in Mo, pH 2.0, 99 °C, showing $[HMoV_9O_{28}]^{4-}$, *trans*- and *cis*-$[Mo_2V_8O_{28}]^{4-}$ as the dominant species in decreasing order of abundance

vanadate,[18] together with the observation[7] that, at least for terminal oxygen, substitution of Mo for V reduces δ_O by a factor of about 1.24. We were able to confirm several of these assignments both by varying the pH (see below) and by obtaining some spectra at 99 °C where the presence of some one-bond couplings to ^{51}V becomes obvious. Simple n.m.r. theory requires that the best-resolved couplings of a given size must arise from the narrowest ^{51}V resonances, and this is a further aid to assignments.

Inevitably, because of the similarities and near-symmetries of structure, there is substantial overlap of some resonances. This made it particularly difficult to distinguish the two (2,8) species. However, we were fortunate to prepare one concentrated solution, at pH 2.0, from which the *cis* isomer had partially precipitated, and in which there was no interspecies exchange at room temperature. The (2,8) assignments in Table 2 are based on this solution. In fact, the only qualitative difference between *cis* and *trans* (2,8) is that the former should have two b-type oxygen resonances, whereas the latter should have only one. That this is indeed the case is shown in Figure 6.

All the shifts in Table 2 are reasonably consistent with the above mentioned $\delta_{O\text{-}Mo} = \delta_{O\text{-}V}/1.24$ factors, suitably scaled in the case of bridging O. A more detailed examination reveals that the shifts of other oxygens increase so as to balance this decrease. Indeed, the sum of oxygen shifts, appropriately weighted, is almost constant for all the species considered, with only *cis*-(2,8) being slightly exceptional at 4% less. This sum is shown in the final row of Table 2. The same sum for other known vanadate and molybdate species, when calculated per oxygen atom, typically differs by 20—30%, but also correlates with structural similarity. It may therefore be a useful qualitative guide to structure.

The shift of oxygen bound to transition metals is well known to correlate with π-bond order.[19,20] Thus one way of viewing the constancy of $\Sigma\delta_O$ for a given structure is to envisage a fixed availability of total π-electron density, which is merely redistributed by substitutions such as Mo for V.

Protonation.—The pK_a of $[HMoV_9O_{28}]^{4-}$, measured both from potentiometry and from ^{51}V shifts, is 2.77. This is fairly close to 3.74,[5] the value for $[H_2V_{10}O_{28}]^{4-}$, as might be expected for two species with the same structure and overall charge. The 1-unit difference is discussed below. The pH dependence of both the vanadium and oxygen shifts is, however, rather different from that for decavanadate, since monomolybdononavanadate is less symmetrical.

Day *et al.*[21] have conclusively shown that decavanadate protonates at either O_b or O_c sites. The clearest marker for this is a lowering of δ_O upon protonation. Our data show that the largest ^{51}V protonation shifts are at peaks (1,9)2 and (1,9)4, and that the only oxygen peaks whose shifts are lowered upon protonation are a′ (−5.5), b (−28.6), and c + c′ (−66 p.p.m.). The latter compound peak has by far the largest shift, unlike decavanadate. Thus although protonation probably occurs at both O_b and O_c, it is now more likely to occur at the O_c site, which is further from the added positive charge of the Mo^{VI}. The same electrostatic repulsion also removes $O_{b'}$ from the competition for H^+. Unfortunately, our data do not similarly discriminate O_c from $O_{c'}$, even after protonation. It seems likely that these two sites are equally favoured.

As noted above, the shifts of the unprotonated oxygens generally increase so as to keep $\Sigma\delta_O$ almost constant. Day *et al.*[21] explain this in electrostatic terms, but his arguments do not exclude the alternative consideration of π bonding, which in any case also fits the molybdenum-substitution data.

*Molybdenum-*95 *N.M.R. Spectra.*—Maksimovskaya and Chumachenko[13] report a resonance corresponding to $[MoV_9O_{28}]^{5-}$ at $\delta_{Mo} = +115$ p.p.m. We find several over-

Table 3. Molybdenum-95 shifts (99 °C) with ^{51}V comparisons

	$[MoV_9O_{28}]^{5-}$	$[HMoV_9O_{28}]^{4-}$	*trans*-$[Mo_2V_8O_{28}]^{4-}$	*cis*-$[Mo_2V_8O_{28}]^{4-}$
δ_{Mo}/p.p.m.	+115.5	+101	+92.4	+110
Nearest V analogue	(0,10)3	H(0,10)3	*cis*-(2,8)3	*trans*-(2,8)3
($\delta_V - \delta_V[VO_4]^{3-}$)/p.p.m.	+25.8	+21.8	+15.7	+25.0

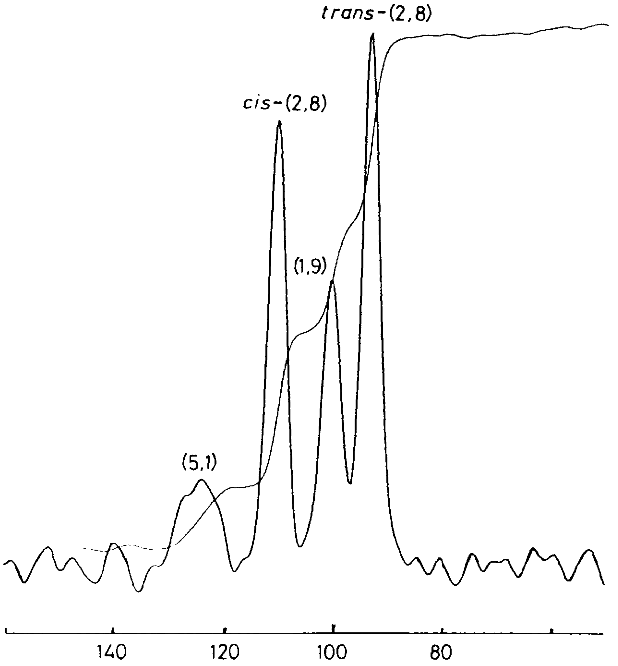

Figure 7. Molybdenum-95 n.m.r. spectrum of a solution 1 mol dm^{-3} in V and 0.25 mol dm^{-3} in Mo, pH *ca.* 1.8, 99 °C. Peak identification as in Table 3, with minor peaks from (5,1) species (see text)

lapping peaks at 99 °C (see Figure 7 for an example) and are able to assign these by correlating the ^{95}Mo n.m.r. spectra with the ^{51}V spectra. The resulting shifts are compared in Table 3 with the nearest equivalent ^{51}V shifts, relative to $[VO_4]^{3-}$. (The latter is at −541.2 p.p.m. on the normal vanadium shift scale.) The two sets of shifts are not strictly comparable, but they do show the same relative shift order and hence confirm the general principle that substitution of Mo for V decreases the chemical shift of the *trans* 'capping' metal atom in the decavanadate structure.

Kinetics of Formation.—We were interested to discover the mechanism by which Mo replaces V in decavanadate. Accordingly, we prepared crystalline, unlabelled decavanadate, and dissolved it in 10% $H_2{}^{17}O$ at pH 5. It does not exchange oxygen with solvent under these conditions, within several hours. In this solution we dissolved $Li_6[Mo_7O_{24}]$, prepared by evaporation at the same pH. This species does exchange oxygen with solvent, almost instantaneously, and gave the anticipated ^{17}O n.m.r. spectrum.[3,19] However, no peaks appeared at this stage from $[MoV_9O_{28}]^{5-}$, which shows that the substitution reaction at this pH is very slow. No doubt this is for the same reason that decavanadate itself exchanges oxygen with solvent on an all-or-nothing basis.[22]

After warming the solution to 100 °C for 1 min, we found that $[MoV_9O_{28}]^{5-}$ had formed to 80% of its equilibrium value, with no evidence whatever of selective labelling. We conclude that the major part of the decavanadate structure cannot be retained during the process of substitution by Mo.

Calculations on E.m.f. Data.—In the e.m.f. calculations we have used the molybdate and vanadate equilibrium constants from refs. 23 and 5 respectively. These studies were also performed in 0.6 mol dm^{-3} Na(Cl) medium.

E.m.f. and combined e.m.f.–n.m.r. data were analysed with the computer program LAKE.[24] A brief description of the program is given in ref. 23.

From the n.m.r. measurements at low Mo:V ratios, $[MoV_9O_{28}]^{5-}$, $[HMoV_9O_{28}]^{4-}$, and two isomeric $[Mo_2V_8O_{28}]^{4-}$ complexes [(15,1,9), (16,1,9), and (16,2,8) in (p,q,r) notation] were firmly established. The n.m.r. spectra had moreover shown that molybdenum-rich species such as (4,2) start to appear by Mo:V $\geqslant$ 0.1. The range where only decavanadate-type structures (Figure 2) exist is thus very restricted. Their equilibrium constants, however, had to be determined. The e.m.f. data clearly confirmed the presence of the two (1,9) species, and gave formation constants with satisfactorily low errors. Because the n.m.r. peaks overlapped, no attempt was made to use n.m.r. integrals in the estimation of these constants. Those of the (2,8) species, on the other hand, could not be determined from e.m.f. data alone. The calculations always showed high standard deviations. For this reason n.m.r. data were used in the refinement of the (2,8) constant (*cis* plus *trans*).

The results from a preliminary calculation on Mo:V $\leqslant$ 0.1 data are given in Table 4 (calculation 1). To obtain the constant for the disubstituted species, the Mo:V range had to be extended, and the medium-ratio species (4,5) and (4,2) had to be inserted also. Supporting n.m.r. evidence for these formulations will be presented in a subsequent paper. Their formation constants, together with that for the sum of the two (2,8) isomers, were determined from combined e.m.f.–n.m.r. data at Mo:V = 1 (calculation 2). These data were weighted so that the residuals from e.m.f. and from n.m.r. contributed equally to the error-squares sum. The high error on the (16,1,9) constant in this calculation is because here the complex is present in only minor amounts. The (2,8), (4,5), and (4,2) constants were then considered to be fixed. A third calculation was then carried out using e.m.f. data at Mo:V $\leqslant$ 0.11 to establish the (1,9) constants. Finally, as a check, the (2,8) constant was once again permitted to vary (calculation 4, using the combined data). No noticeable change occurred in this calculated formation constant. Remaining residuals are small and the pK_a value of the monoprotonated (1,9) species (2.8) is in perfect accordance with the pH dependence of the chemical shift curves shown in Figure 3.

Species Distribution.—The constants from calculation 3 have been used when calculating and plotting distribution diagrams with the additional computer program SOLGASWATER.[25] In Figure 8(*a*) and (*b*) is shown the distribution of vanadium in different species for the Mo:V ratios 0.05 and 0.25. To simplify the diagrams, species that contain less than 5% of the total vanadium concentration have been omitted. For clarity only the sum of the different metavanadate species is shown and in Figure 8(*b*) only the sum of the decavanadate species as well. The monosubstituted species can be seen to be relatively dominant. At Mo:V = 0.05 [Figure 8(*a*)], which is approximately half the Mo:V ratio in MoV_9 (0.11), almost half the vanadium is bound in the MoV_9 species in the medium-acidity

Table 4. Results from calculations on e.m.f. data in the range pH 1.5—7

Calculation	Mo:V	No. of points		$\sigma(H)^{a}$/ mmol dm^{-3}	log $\beta_{p,q,r}(3\sigma)^{b}$			
		e.m.f.	n.m.r.		(15,1,9)	(16,1,9)	(16,2,8)	p*K*(16,1,9)
1	$\leqslant$0.1	61		0.18	124.41(9)	137.22(8)		2.82
2	1	36	9		134.47(9)	137.43(31)	132.97(18)	2.96
3	$\leqslant$0.11	85		0.23	134.56(10)	137.33(16)	132.97	2.77
4	1	36	9		134.56	137.33	132.96(9)	2.77

[a] Standard deviation between the calculated and measured hydrogen-ion concentrations. [b] The 3σ values given in parentheses refer to the last decimal place given. When no 3σ is given the constant in question has not been allowed to vary from the value obtained in the preceding calculation.

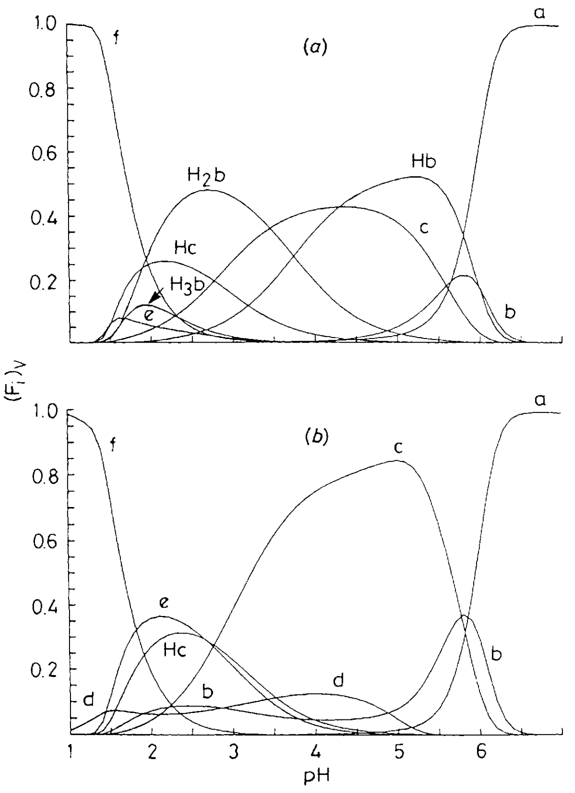

Figure 8. Diagrams showing the distribution of vanadium as a function of pH. The quantity $(F_i)_V$ is defined as the ratio between the vanadium in a species to the total vanadium. In the calculations, equilibrium constants from Table 4 (calculation no. 3) and from refs. 5 and 23 were used. For clarity, species with $(F_i)_V < 0.05$ have been omitted. Mo:V ratio is 0.05:1 (*a*) and 0.25:1 (*b*). Species: a = $[H_2VO_4]^-$ + $[V_4O_{12}]^{4-}$ + $[V_5O_{15}]^{5-}$; b = $[V_{10}O_{28}]^{6-}$; Hb = $[HV_{10}O_{28}]^{5-}$; H$_2$b = $[H_2V_{10}O_{28}]^{4-}$; H$_3$b = $[H_3V_{10}O_{28}]^{3-}$; c = $[MoV_9O_{28}]^{5-}$; Hc = $[HMoV_9O_{28}]^{4-}$; d = species with higher Mo:V ratios; e = *cis*-plus *trans*-$[Mo_2V_8O_{28}]^{4-}$; f = $[VO_2]^+$

range, and at Mo:V = 0.25 [Figure 8(*b*)] $[MoV_9O_{28}]^{5-}$ predominates except at low pH. The (16,2,8) species are sufficiently acidic to experience competition from the very stable $[VO_2]^+$ ion. All the polyanions are completely decomposed at high acidity (pH < 1.2). Substitution of V^V in decavanadate with Mo^{VI} decreases the minus charge by one unit and thus makes the substituted species a more 'acidic' complex [equation (2)].

$$[V_{10}O_{28}]^{6-} + Mo^{VI} \longrightarrow [MoV_9O_{28}]^{5-} + V^V \quad (2)$$

From an electrostatic point of view the monoprotonated decavanadate species, $[HV_{10}O_{28}]^{5-}$ [(15,0,10) in (*p,q,r*) notation], should behave similarly to $[MoV_9O_{28}]^{5-}$ (15,1,9) and exist in the same pH range. This is, however, not quite true. Molybdenum(VI) moves the 'acidity' range to lower pH than $H^+ + V^V$, as seen in the distribution diagrams. The order of 'acidity' is $[Mo_2V_8O_{28}]^{4-}$ (16,2,8) > $[HMoV_9O_{28}]^{4-}$ (16,1,9) > $[H_2V_{10}O_{28}]^{4-}$ (16,0,10). This probably implies that the additional positive charge is more readily accepted on the periphery of the anion.

Conclusions

It has been appreciated for some time that the decavanadate structure possesses unusual thermodynamic and kinetic stability. The reasons for this are not yet fully understood, although they are undoubtedly related to the tendency of vanadium(v) to form just one or two short bonds to oxygen.[4,26] The data presented here confirm this stability, for the same structure is shown to withstand up to two substitutions by Mo without significant structural effect on the shifts of the remaining vanadiums. It is also shown to be kinetically inert, and to dominate the solution chemistry of molybdovanadates in the entire vanadium-rich region.

In an earlier paper[7] we presented a justification for describing as 'capping' the MO units lying out of the principal plane of 3 × 2 fused MO_6 octahedra. Our argument implied that these units would be the easiest to replace, and this is confirmed by the present results. It is more of a surprise to find that the *cis*-(2,8) species is almost as stable as the *trans* one, for on electrostatic grounds it should be the least stable of the three possible cap-substituted (2,8) species. The explanation will probably be linked with the corresponding counter-intuitive observation that the preferred (4,2) tungstovanadate isomer has *cis* rather than *trans* vanadium atoms.[15]

This study also emphasised the importance of combining n.m.r. and potentiometric measurements. The structure similarities of the four decavanadate-type anions means that their vanadium resonances overlap, and also that their pK_a values are mutually related. The overlap of resonances obscures the n.m.r. quantitation and that of pK_a values leads to unreliable potentiometric fits as well as the inability to detect isomers. However, the combined data give a secure conclusion.

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