Aqueous tungstovanadate equilibria

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A combined equilibrium study of tungstovanadates involving potentiometry and ^{51}V, ^{183}W and ^{17}O NMR spectroscopy has been able to identify 11 main species, giving their formation constants and pK_a values where relevant. Tentative identification was also made of two other non-equilibrium species at lower pH values, in addition to those with a V-centred Keggin structure. The ^{51}V shifts of the unprotonated hexametalate anions fall into a rational pattern, and the formation constants are all higher than those of the corresponding molybdovanadate species, where comparisons are possible.

Although several polyoxotungstovanadate species have been known for some time,[1] the interactions of aqueous tungsten(VI) with vanadium(V) have not been studied systematically over a wide range of pH, and attention has been concentrated on the dominant species only. The most prominent of these are $[W_5VO_{19}]^{3-}$ **1** (see Table 1) at low pH and *cis*-$[W_4V_2O_{19}]^{4-}$ **2** above pH 3. Both have the Lindqvist double-octahedron structure.[2–4] The latter anion protonates with pK_a about 1.5 units lower than for the corresponding molybdovanadate species *cis*-$[Mo_4V_2O_{19}]^{4-}$. Owing to this tendency for tungstovanadates to protonate less readily than molybdovanadates, the trisubstituted species *fac*-$[W_3V_3O_{19}]^{5-}$ is also known at higher pH,[5] even though its molybdenum analogue is unknown. The evident preference for the V atoms to be mutually adjacent is confirmed at lower pH by a range of V-centred α-Keggin species.[5] A metatungstate Keggin species with one substitution of V for W, $[H_2W_{11}VO_{40}]^{7-}$, has also been described, but only characterised by NMR spectroscopy and not crystallographically.[6,7]

At higher pH values, say 5–7, one might also expect to find species with the decavanadate structure, such as $[WV_9O_{28}]^{5-}$ **6**, by analogy with $[MoV_9O_{28}]^{5-}$, and indeed this species has been proposed by Maksimovskaya and Chumachenko[8] on the basis of ^{51}V and ^{17}O NMR spectra, albeit with an incomplete assignment of resonances. Its molybdenum analogue also protonates,[9] with pK_a = 2.77, and at pH < 4 it can also accept a second substitution of Mo for V, to form both *cis* and *trans* dimolybdooctavanadates. One would like to know if the corresponding chemistry takes place with tungstovanadates.

One reason why tungstovanadates have proved hard to study is that they are slow to equilibrate. This inhibits their study by equilibrium potentiometry, so that no absolute formation constants have yet been published for any tungstovanadates. In the present study all the solutions above pH 3.5 reached equilibrium after 2 d at 25 °C. This was checked by repeated measurements. The attainment of equilibrium could not be speeded by initial warming. However, with solutions starting at lower pH values, further changes were generally detected in *e.g.* the ^{51}V NMR spectra after 5–10 d, and these were not complete even after 3 months. Most of the present study concerns the species at equilibrium, although those others which are slowest to form are discussed in a final section. Observations were made primarily by ^{51}V NMR, although ^{17}O and ^{183}W NMR spectra were also obtained for species with high concentration.

Experimental

Spectra

Initial solution-state NMR spectra were obtained at 105.5 (^{51}V), 54.2 (^{17}O) and 16.65 (^{183}W) MHz on a Bruker WH400 spectrometer and at 20 or 89 °C in lightly deuteriated 0.600 mol dm^{-3} aqueous Na(Cl). Typical parameters for the spectra were (^{51}V) spectral width 28 kHz, acquisition time 0.147 s, no relaxation delay, 8k data points in both domains, 2000 transients, 35° pulse angle. The corresponding values for ^{17}O NMR spectra were 83 kHz, 0.025 s, no relaxation delay, 4k points, 20 000 transients, isotopic enrichment to *ca.* 5% by solvent exchange with typically 1 d allowed for reaction, 35°; for ^{183}W, 20 kHz, 1.64 s + 1 s delay, 64k points, 30 000 transients, 30°. Further ^{51}V spectra were obtained at 131.6 MHz on a Bruker AMX500 spectrometer, at 25 ± 0.5 °C in undeuteriated medium, for precise comparison with potentiometric data at the same temperature and with earlier data on vanadate equilibria.[10,11] In this case the field–frequency stabilisation was *via* annular D_2O held between the 8 mm sample tube and a 10 mm outer tube. Peak areas in ^{51}V NMR spectra could typically be measured to within 10%, with deconvolution fitting (Bruker UXNMR/P). Oxygen peak areas were reliable typically within 20%. The ^{51}V chemical shifts, even at 89 °C, were referenced to external capillary $VOCl_3$, and the ^{183}W shifts to external 2 mol dm^{-3} $[WO_4]^{2-}$. The spectrometer's temperature controller was indirectly calibrated *via* a Comark thermocouple inserted into a dummy sample, and itself separately calibrated in melting ice and boiling water.

Solutions for quantitative pH and NMR studies

For the 25 °C measurements, sodium chloride (E. Merck p.a.) was dried at 180 °C and used without further purification to make the 0.600 mol dm^{-3} Na(Cl) medium with boiled distilled water. Dilute solutions of HCl (E. Merck p.a.) were standardised against tris(hydroxymethyl)aminomethane (Tris, Sigma Chemical Co.). The salt $Na_2WO_4{\cdot}2H_2O$ (E. Merck p.a.) was recrystallised before preparing a stock solution, which was standardised by evaporation to anhydrous solid at 120 °C; $NaVO_3{\cdot}2H_2O$ (E. Merck p.a.) was dissolved in hot water, then cooled, filtered through G4 porous glass, and also standardised by evaporation to anhydrous solid. Individual 'point solutions' were mixed and allowed to equilibrate for at least 2 d at 25 °C. The pH range was 1.8–8.2, with the individual pH values as shown in Figs. 1, 2 and (in part) 5. The W:V ratios were 17:68, 30:60 and 50:50 (mmol dm^{-3}). The pH was measured with an Ingold U402-M6-S7/100 combination electrode, calibrated using solutions of known $[H^+]$ in the same medium.

Computation

Equilibrium analysis of pH, ^{51}V shift and integral data was by the least-squares program LAKE.[12] This new program can simultaneously treat data from more than one method, and hence can also estimate the individual shifts of species contributing to a protonation equilibrium, even though only mixtures are present within their stability range. Distribution diagrams were constructed using the program SOLGASWATER.[13]

Results

Fig. 1 shows the variation of ^{51}V peak positions with pH at 25 °C, for fully equilibrated solutions. Similar curves were obtained at 20 and 89 °C. The shifts, with respect to external capillary $VOCl_3$, showed typical temperature dependences of $+0.08$ to $+0.11$ ppm K^{-1}.[14] In Fig. 1, resonances arising from one anion, *i.e.* having constant integer area ratios, are identified by a single symbol; individual peak assignments were given in a preliminary communication,[15] in which the V-atom connectivities were established by two-dimensional $^{51}V-^{51}V$ correlation spectroscopy (COSY) experiments showing almost all the two-bond V–V couplings. Curved lines arise from protonation, because this is the only fast-exchange process that occurs in these aqueous tungsten-containing species. The pK_a value of the appropriate anion could be determined from all of these curves, together with the equilibrium data, even though several of the species lose stability upon protonation. The quality of the Henderson–Hasselbalch fits, illustrated in Fig. 2, is good even for the minor species, and the resulting data are given in Table 1. In the cases of compounds **2** and **6** in this table, the pK_a values could also be determined from the ^{17}O NMR spectra. These give a more reliable indication of the main site of protonation, because an O atom always moves to lower shift upon protonation, whereas the protonation shift of metal atoms is less predictable. Typical ^{51}V and ^{17}O NMR spectra are shown in Figs. 3 and 4 respectively.

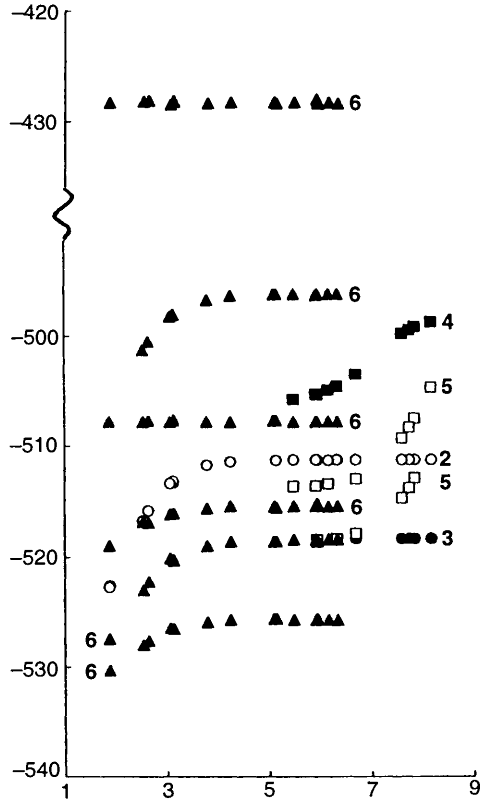


Fig. 1 Dependence of ^{51}V NMR resonances on pH, at 25 °C. The resonances of the tetrahedral isopolyvanadate species are not shown. Species numbering as Table 1

At least 98% of the V in the region pH 3.5–8.1 and in the more dilute, fully equilibrated solutions can be accounted for in terms of known vanadate and tungstovanadate species. The major species could all be identified by their peak-area ratios, and also in three cases by their shifts. At pH < 3.5 the spectra became too complex for the accurate evaluation of peak areas, because many different Keggin species form. However, the assignments at pH > 3.5 were confirmed by equilibrium calculations. Fig. 5(*a*)–(*c*) shows the results of these calculations: such fits could not be obtained if any species had been assigned an incorrect formula. They also demonstrate that even minor species, as in

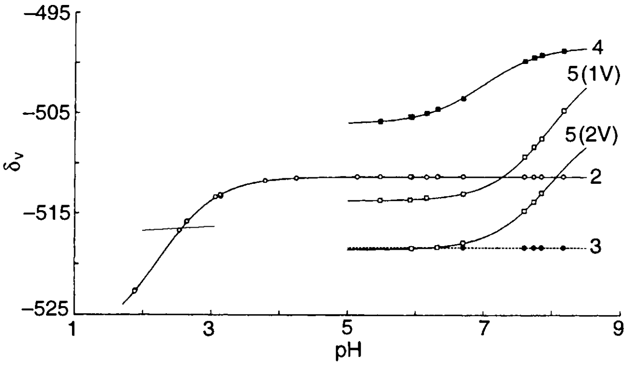


Fig. 2 Expansion of Fig. 1 with fitted titration curves

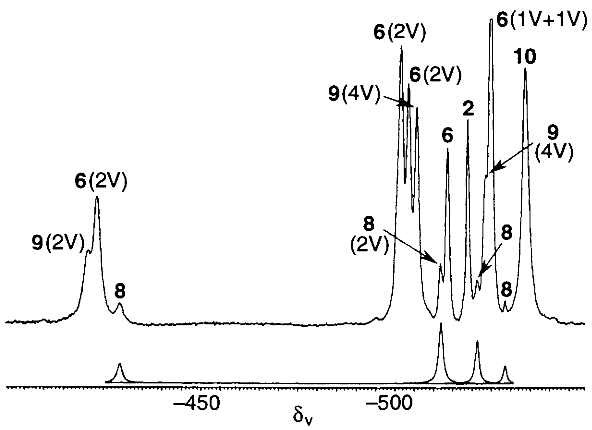


Fig. 3 Typical ^{51}V NMR spectrum at pH 1.6, showing four minor resonances (**8**) deconvoluted. They possibly arise from $[W_4V_5O_{27}]^{5-}$. Other labels as Table 1, plus decavanadate, here as $[H_2V_{10}O_{28}]^{4-} \rightleftharpoons [H_3V_{10}O_{28}]^{3-}$ **9** and $[VO_2]^+$ **10**

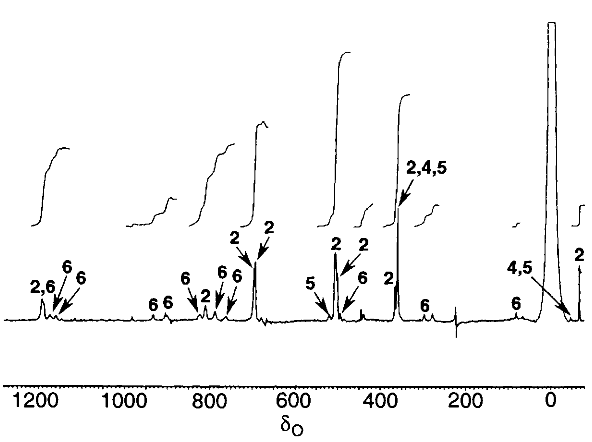


Fig. 4 Typical integrated ^{17}O NMR spectrum of a solution at 20 °C, 250 mmol dm^{-3} in both W and V. Species numbering as Table 1

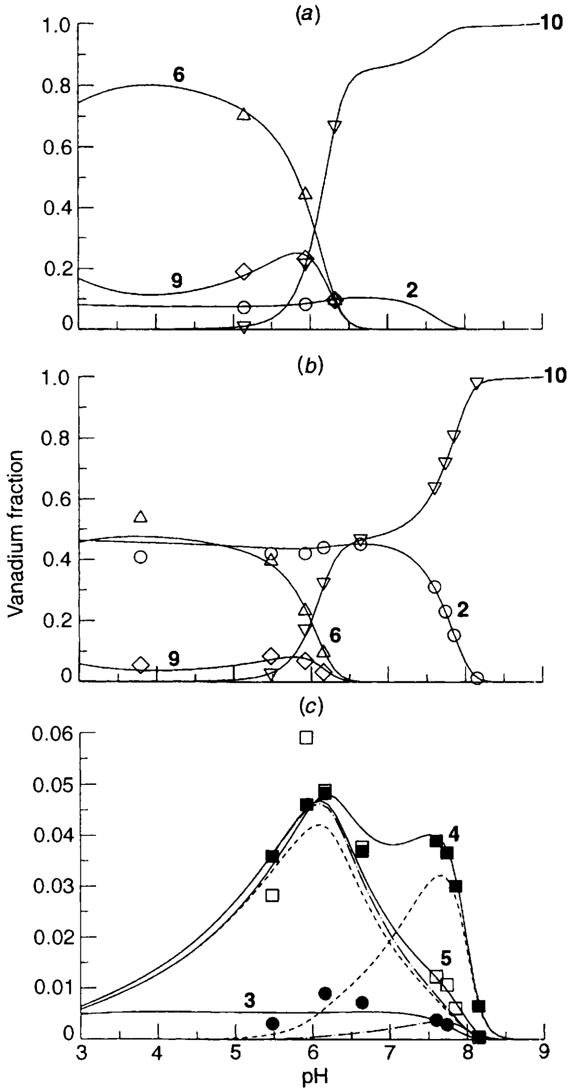


Fig. 5 Distribution diagrams of mole fraction (as V) present *vs.* pH, for various metal concentrations at 25 °C. Curves are calculated abundances, symbols are experimental data. Species numbering as in Table 1, plus decavanadate **9** and other isopolyvanadates **10**. W:V = 17:68 mmol dm^{-3} (*a*) (major species only), 50:50 (*b*) (major species only) and 50:50 (*c*), vertically expanded to show minor species, with added dashed lines to indicate their calculated breakdown into protonated and unprotonated anions

Fig. 5(*c*), can yield fairly reliable equilibrium constants once the major species have been identified. These constants are listed in Table 1. In this equilibrium analysis H^+, $[WO_4]^{2-}$ and $[H_2VO_4]$ were chosen as components and the formation reactions were then written in the general form (1).

$$pH^+ + q[WO_4]^{2-} + r[H_2VO_4]^- \rightleftharpoons [(H)_p(WO_4)_q(H_2VO_4)_r]^{p-2q-r} \quad (1)$$

The isopolyvanadate system has been studied previously in the same ionic medium[10] and the formation constants from a recent high-field ^{51}V NMR study in the same medium are reported in ref. 11. The isopolytungstate system has not been studied in this medium. However, at the low W:V ratios used here, no isopolytungstates could be detected because the tungstovanadate anions had very high formation constants. This simplified the analysis considerably. Also, because the corresponding molybdovanadate ternary system has already been studied in the same medium, it is now possible to compare the corresponding equilibrium constants directly. It is convenient to consider each species in turn, using the species numbering in Tables 1 and 2.

Hexametalate species $[W_5VO_{19}]^{3-}$ 1

This ion has already been identified in acetonitrile by Klemperer and Shum,[3] and in aqueous solutions by Leparulo-Loftus and Pope.[5] The shifts and assignments are given in Table 1; they agree well with the values reported previously. It appears only below pH 3 in aqueous solution.

cis-$[W_4V_2O_{19}]^{4-}$ and $[HW_4V_2O_{19}]^{3-}$ 2

These anions dominate the spectra under most conditions. Their shifts are in full accord with those reported by Leparulo-Loftus and Pope[5] (^{51}V) and by Maksimovskaya and Chumachenko[8] (^{51}V, ^{17}O). They are reported in Table 1 for ease of comparison with less well established species. The fitted pK_a value is 2.23 at 25 °C and 2.2 at 89 °C. This may be compared with 3.74 for *cis*-$[Mo_4V_2O_{19}]^{4-}$.[16] The comparatively large effect of protonation on the ^{51}V shift, −16.5 ppm, supports Kazanskii's proposal[17] that the anion protonates at the edge oxygen bridging the two V atoms, as one might predict on electrostatic grounds. The resonance of the oxygen bridging the two V atoms also shifts to lower frequency in this solvent, which confirms the above protonation site and the earlier conclusions of Klemperer and Shum,[3] from non-aqueous solutions. At the higher temperature the ^{51}V resonance is sufficiently narrow to permit an estimate of ^1J[VO(terminal)] of *ca.* 18 Hz.

trans-$[W_4V_2O_{19}]^{4-}$ and $[HW_4V_2O_{19}]^{3-}$ 3

Fig. 5(*c*) shows that a much smaller ^{51}V resonance covaries in area with that of the anion **2**, but has only 1.2% of its peak area. Fig. 6 shows that it is present under conditions when the only other species is the *cis* isomer. It also shows no couplings to other resonances, in COSY spectra. Its pK_a could only be estimated at 89 °C; it is 2.5, which is only a little higher than that of its isomer. However, its ^{51}V resonance shifts by only *ca.* −10 ppm on protonation, compared with −16.5 ppm above. Unfortunately, its concentration is insufficient for ^{17}O NMR spectroscopy. The implied assignment is justified below.

fac- and *mer*-$[W_3V_3O_{19}]^{3-}$ 4, 5

The existence of anion **4** has been tentatively claimed by Leparulo-Loftus and Pope,[5] from the stoichiometry of its decay, and from its single ^{51}V resonance. Its shift, and that of its monoprotonated form, are given in Table 1. Fig. 2 shows that it undergoes protonation at pH 7.0.

Two further peaks, at δ −498.9 and −505.2 (pH < 6) covary in intensity with that of **4**, and have a combined peak area very close to that of **4**. Also, these peaks are themselves in a constant area ratio of 1:2, and, unlike **4**, they show a strong mutual coupling in COSY spectra. They each show a pK_a of 8.0. These observations are entirely consistent with a *mer* isomer, **5**, as argued in a preliminary communication.[15] Some ^{17}O shifts were obtained for both anions, and these are listed with proposed assignments in Table 1. They differ significantly from those in an earlier report,[18] and partially support the above hexametalate formulations.

Decametalates: $[WV_9O_{28}]^{5-}$ and $[HWV_9O_{28}]^{4-}$ 6

The presence of these two species is apparent from the data in Fig. 1, given that the three resonances with highest shift each have twice the areas of each of the three resonances with lowest shift. The peak assignments were obtained unambiguously from a two-dimensional COSY spectrum at 89 °C, as presented in a preliminary communication.[15] The shifts are similar to those of $[MoV_9O_{28}]^{5-}$, and all the data are solely consistent with a

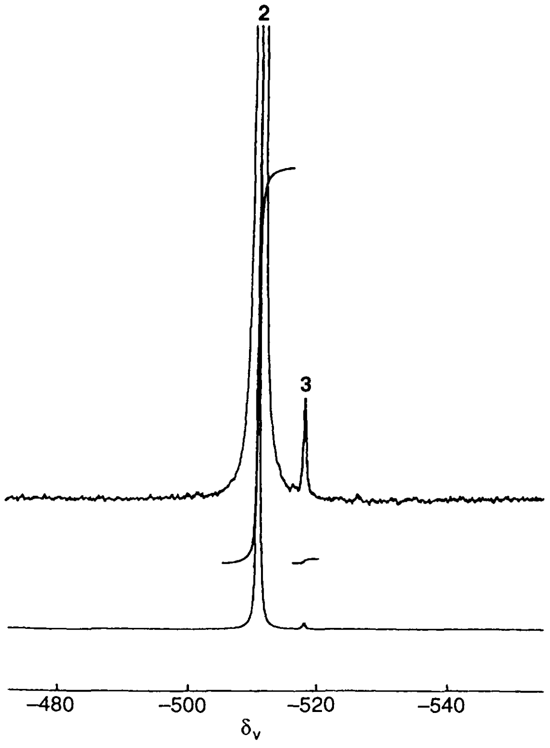


Fig. 6 Vanadium-51 NMR spectrum of a solution at pH 7.0, 80 mmol dm^{-3} in W and 20 mmol dm^{-3} in V at 20 °C, showing solely the species **2** (major) and **3** (minor)

structure of the decavanadate type, with the substitution of W at a 'capping' position. Surprisingly, the capping V having lowest shift, and also least like the corresponding shift of decavanadate, arises in fact from the position furthest from the W atom, and hence with a local environment most like that in decavanadate.

The ^{51}V and ^{17}O shifts of the unprotonated decametalate species were reported at lower field by Maksimovskaya and Chumachenko,[8] but not fully assigned. The higher field used in the present measurements has allowed more peaks to be resolved, and so has led to some reassignment of these spectra, as listed in Table 1. Here, the added signs in parentheses indicate the oxygen shift change upon protonation. Our assignments correspond closely in their pattern to those for the molybdenum analogue, although, as expected, the general effect of the W atom is to lower the shifts of the oxygens to which it is attached, more than does Mo. Unfortunately, the protonation is not complete within the stability range of $[HWV_9O_{28}]^{4-}$. However, the pK_a may be shown by curve-fitting to be 2.15 at 25 °C (*cf.* 2.77 for the Mo analogue at 20 °C). This difference between W and Mo has the same sign as with species **2**, and can be explained in terms of the differing M–O bond strengths.[19] The only O atoms with a significant lowering of shift upon partial protonation are c and c′, using the earlier labelling system. These are the bridging edge oxygens at the opposite end of the decavanadate structure from the tungsten substituent, as one might expect on electrostatic grounds. There is only slight evidence for protonation at the b sites, which bridge the two capping V atoms, namely a shift of −2 ppm compared with −12 ppm at c + c′.

Dodecametalates with Keggin structures: α-$[H_2W_{11}VO_{40}]^{7-}$ 7

This species has been characterised by Pope and co-workers[6] on the basis of single resonances in ^{1}H and ^{51}V NMR spectra. We have observed that, although it does not form to any appreciable extent in the 2-day pseudo-equilibrium mixtures, it becomes a major species in aqueous solution after several weeks at room temperature. As reported in a preliminary communication,[16] it has six ^{183}W resonances, centred around the δ_W −123 shift of α-$[H_2W_{12}O_{40}]^{6-}$. The peak-area ratios are 2:2:1:2:2:2, and the shifts are far more consistent with an α-Keggin structure than with any other isomer of this. No other mixed-metal dodecametalates were found to form. The protonation state of this anion could not be determined by our measurements, so the formula given above is notional in this respect.

Unassigned species 8

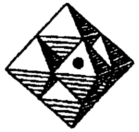
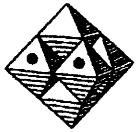
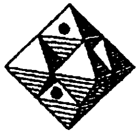
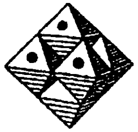
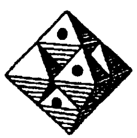
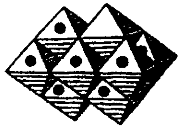
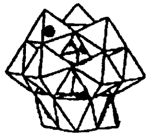
Four further resonances appear together, with constant area ratio, at 20 °C and pH ≈ 2.5, in solutions 17 mmol dm^{-3} in W and 68 mmol dm^{-3} in V. They are shown in Fig. 3, together with an attempted deconvolution, and their pH-dependent shifts are listed in Table 2. It is not likely that these resonances arise from analogue(s) of *cis*- and *trans*-$[Mo_2V_8O_{28}]^{4-}$, even though their shifts are similar,[9] because these molybdovanadates have charges too low for protonation to occur. If anything, one would expect any corresponding tungstovanadate anion to have an even lower pK_a value, by analogy with species **2** and **6**. It is more likely that they arise from the tungsten analogue of $[Mo_4V_5O_{27}]^{5-}$ and its monoprotonated form (pK_a = 3.74), but unfortunately the concentration is too low for confirmatory ^{17}O and ^{51}V–^{51}V COSY measurements, so that other formulations cannot be ruled out. Table 2 shows that the ^{51}V shifts of this possible molybdenum analogue are similar to those of the unknown WV species, but with a slightly greater spread. A unique feature of the Mo_4V_5 species is that the Mo-centred octahedra cluster at one end of the anion, rather as in heptamolybdate, and the V-centred octahedra at the other end, as in monomolybdononavanadate.[9] This eases the size disparity of the two types of octahedron. It is possible that it may thus ease sufficiently to permit the analogous fusion of V- and W-centred octahedra, because both heptatungstate and monotungstononavanadate are also known species.

Ageing of solutions

The very slow formation of anion **7** was mentioned above. The time course of this ageing process is shown in Fig. 7, for a relatively strong solution, 1.67 mol dm^{-3} in W and 0.33 mol dm^{-3} in V. For clarity, this figure omits species **2**, which was present in the approximately constant proportion of 80% of the dissolved V. No precipitation occurred, but the pH of this solution rose from 2.65 to 5 over the 100 d. A few very minor peaks have been omitted, and the lines serve only to guide the eye. It is immediately clear that the ageing process is complex. The only other recognisable species is **1**. Species **2** forms rapidly, in high proportion, but then about 10% of it decomposes within a few hours, to give mainly **1** at first. Thus **2** is the kinetically stable species. After this, **1** decays by a much lower proportion, *ca.* 1%, over 2–3 weeks, and two new resonances, labelled **a** and **b**, grow instead, at the same rate. After 2 months these also largely decay, again at the same rate, and several other resonances take their place at similar rates, notably **c**, **d** and those of **7**. However, the area ratios **a**:**b** and **c**:**d**, though constant, are not precisely integral. We were unable to detect any couplings involving these resonances. A typical spectrum is shown in Fig. 8. The resonances probably arise from a considerable variety of V-centred Keggin species, with partially overlapping resonances. The proportion of V in these species is likely to increase as the pH rises, and as the formation of **7** releases V. The decays of **a** and **b** probably involve replacements of octahedral W by V, for this is expected to increase the shifts of the central, tetrahedral V,[5] from *ca.* δ −560 in $V^{tet}V^{oct}_2$ anions to *ca.* δ −554 in $V^{tet}V^{oct}_3$ anions, at 20 °C. The observed shifts are respectively δ −561.9 and −555.9 for resonances **c** and **d**, with most of the more minor resonances at slightly higher frequency.

In a further experiment the initial proportion of anion **1** was

Table 1 Species, shifts, pK_a values and formation constants at 25 °C in 0.600 mol dm^{-3} Na(Cl) medium

	Formula	Proposed structure	pK_a	log β ± 3σ[a]	δ_V	δ_W	δ_O					
							W_6O	WOW	WOV	WO	VOV	VO
1	$[W_5VO_{19}]^{3-}$				−526.4		−76.2	385 403	544.4	739.3		1235
2	*cis*-$[W_4V_2O_{19}]^{4-}$			56.67 0.07	−511.3	69.0	−68.2	360.0 366.3	502.0 507.8	693.9 697.4	810.9	1191
	cis-$[HW_4V_2O_{19}]^{3-}$		2.23	58.90 0.07	−527.8							
3	*trans*-$[W_4V_2O_{19}]^{4-}$			54.75 0.43	−518.4							
	trans-$[HW_4V_2O_{19}]^{3-}$		2.5		*ca.* −528							
4	*fac*-$[W_3V_3O_{19}]^{5-}$			41.56 0.09	−498.3							
	fac-$[HW_3V_3O_{19}]^{4-}$		6.99	48.55 0.09	−506.0		−51	349	502[b]	676[c]	811[b]	1190[b]
5	*mer*-$[W_3V_3O_{19}]^{5-}$			40.60 0.11	−498.9 (1V) −505.2 (2V)							
	mer-$[HW_3V_3O_{19}]^{4-}$		7.99	48.59 0.11	−513.7 (1V) −518.6 (2V)		−51	355	480[b] 506[b] 517.5	669[c]	811[b]	1190[b]
6	$[WV_9O_{28}]^{5-}$			65.52 0.03	−428.2 (2V) −496.2 (2V) −507.8 (2V) −515.4 (1V) −518.6 (1V) −525.7 (1V)	74.5	81.8 *b*	297.5[d]	440.0[e] 495	762.1	788(−)[f] 788(−) 824 824 905(+) 934	1160 1175(+) 1175(+) 1191(+)
	$[HWV_9O_{28}]^{4-}$		2.15	65.67 0.04	−428.3 (2V)[g] −514.0 (2V) −507.8 (2V) −520.9 (1V) −532.6 (1V) −533.0 (1V)							
7	α-$[H_2W_{11}VO_{40}]^{7-}$ [h]				−544.3	−111.6 (2W) −119.8 (2W) −121.3 (2W) −121.5 (1W) −124.0 (2W) −132.7 (2W)						

● Vanadium site. [a] Formation constant as described in the text. [b] Obscured by large, nearby resonances. [c] Assignment may be reversed. [d] WOV_2. [e] VOV_2. [f] Shift change on protonation. [g] In the same shift order as above. [h] Protonation state not determined. δ(H) 6.0.

Table 2 Comparison of vanadium-51 NMR shifts of the unknown tungstovanadate species **8** with those of the $[Mo_4V_5O_{27}]^{5-}$ anion

$\delta(^{51}V)$	
8	$[Mo_4V_5O_{27}]^{5-}$
−428.7* (1V)	−440* (1V)
−509.2 (2V)	−491.6 (1V)
−520.1 (1V)	−501.6 (1V)
−528.6 (1V)	−504.4 (1V)
	−518.6 (1V)

* All shifts at 20 °C.

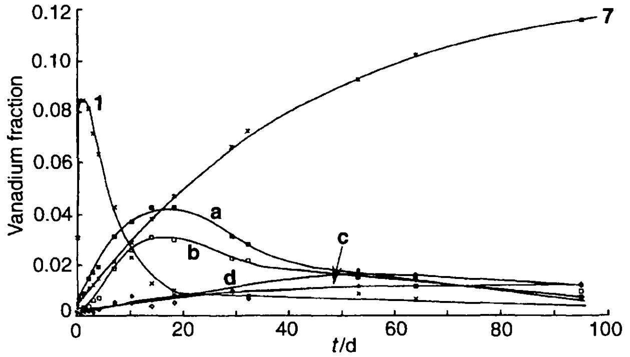


Fig. 7 Slow equilibration of a solution 1.67 mol dm^{-3} in W and 0.33 mol dm^{-3} in V, monitored by ^{51}V NMR spectroscopy. Initial pH 2.65, giving pH 5.0 after 100 d. For clarity, species **2** (*ca.* 80% of the V present) and also several very minor resonances have been omitted

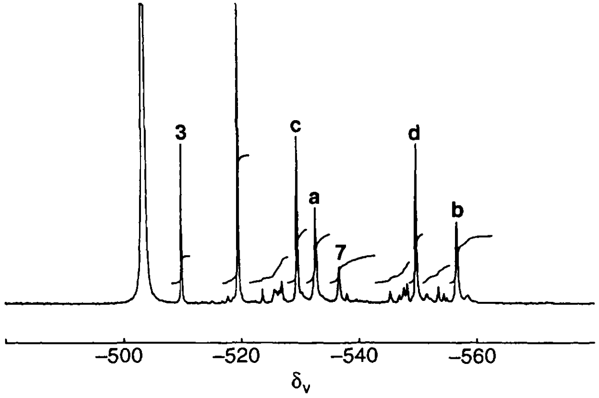


Fig. 8 Vanadium-51 NMR spectrum of a solution initially at pH 2.8, 400 mmol dm^{-3} in W and 100 mmol dm^{-3} in V, aged for 3 months at 20 °C and then briefly raised to 89 °C before cooling again. Species numbering as Table 1; unlabelled small peaks arise from V-centred Keggin species

increased to *ca.* 17% by heating, followed by immediate cooling. This increase probably occurs because the higher temperature converts some of the isopolytungstates present into monotungstate. Following it, **1** then decays about twice as rapidly as before, *i.e.* over about 2 d. The formation of **1** from **2** raises the pH of the solution by absorption of protons; this was confirmed by direct measurement of the pH. The increase in $[OH^-]$ probably then speeds the initial room-temperature conversion of **1** into **7**, *etc.*

Discussion

trans-$[W_4V_2O_{19}]^{4-}$ and $[HW_4V_2O_{19}]^{3-}$

Leparulo-Loftus and Pope[5] have shown that the edge sharing of VO_6 octahedra, in vanadotungstates with Keggin structures, leads to increases of *ca.* 5–20 ppm in the vanadium shift. They also show that although this structural motif is favoured it does not exclude the possibility of other geometries. Thus one might anticipate the presence of a minor *trans* isomer, with a somewhat lower vanadium shift than that of the *cis*. We observe a shift 7.1 ppm lower for our proposed *trans* isomer, and this is analysed quantitatively in the following section. The *trans* formulation is also supported by the protonation data. Since the *cis* isomer has one dominant site for protonation, at the edge O bridging the two V atoms, it is logical that the *trans* isomer should have eight protonation sites, at all the VOW bridges. Each site is likely to be less basic than the unique VOV site in the other isomer, but this will be offset by the increased statistical factor. Thus we might anticipate a similar pK_a, as is observed. Also, protonation at one of these eight sites will now affect only one V, whereas protonation at VOV affects both. We therefore anticipate, and observe, an approximate halving of the vanadium shift upon monoprotonation.

mer-$[W_3V_3O_{19}]^{5-}$

The coexistence of the *mer*-$[W_3V_3O_{19}]^{5-}$ isomer with the *fac* is not surprising. It has two edge-sharing VO_6 octahedra, a feature known to be favoured, together with a more spreadout distribution of metal-ion charge than that of its isomer. The shifts of its V atoms, relative to the *fac* isomer, are also very much what might be predicted from the above principle that the vanadium shift increases with increased edge sharing. Indeed, the shifts of the various unprotonated hexametalate species may all be predicted by a simple analysis similar to that proposed recently for mixed $W_nMo_{4-n}V_2$ hexametalates.[20] One starts from a base shift of δ −525.92, essentially that of **1**, and then adds 13.7 ppm when V replaces a W *cis* to the V under observation, and +7.2 for the corresponding *trans* replacement. The resulting calculated shifts are given in italics after the observed shift: **2**, δ −511.3, *−512.1*; **3**, −518.4, *−518.6*; **4**, −498.3, *−498.5*; **5**, 2V, −505.2, *−505.0*; **5**, 1V, −498.9, *−498.5*. Thus the shifts form a very regular series. The corresponding shift increments for substitutions of Mo for W are (*cis*) +5.6 and (*trans*) −1.1 ppm.

One also notes that the protonation shifts of all the V atoms in anions **4** and **5** are close to those found for **2** and **3**, as expected. However, the decrease in pK_a of 1.0 on going from **5** to **4** is harder to explain. The formation constants in Table 1 show that it arises from the increased stability of the unprotonated anion **4**, and this in turn may be explained by the greater number of two-oxygen edges shared between identical metal atoms in this isomer. A similar influence of edge sharing upon stability has been noted in the $W_nMo_{4-n}V_2$ isomers.[20] Protonation renders the metal atoms no longer identical.

Formation constants

In general, one is not surprised to find that tungstovanadates form similar species to molybdovanadates, but in different proportions. The non-existence of ditungstooctavanadates can be attributed to the lower pK_a value for **6** and to greater competition from **2**. The same factors allow the formation of **4** and **5** at pH 5–7, given that their structure has approximately the same bonding character as in **2**.

Four of the log formation constants given in Table 1 may be compared directly with those of the corresponding molybdovanadate anions. They are *cis*-$[W_4V_2O_{19}]^{4-}$ 56.67 (molybdenum equivalent 44.48), $[HW_4V_2O_{19}]^{3-}$ 58.90 (48.22), $[WV_9O_{28}]^{5-}$ 65.52 (63.05) and $[HWV_9O_{28}]^{4-}$ 67.67 (65.82). Thus the tungsten complexes are all more stable than the molybdenum complexes. This is consistent with their lower lability, and with the greater stability of heptatungstate with respect to heptamolybdate. (Although the isopolytungstate formation constants have not been recorded, it is known that both hepta- and dodeca-tungstate start to form from the monomer at pH *ca.* 8, compared with pH *ca.* 7 for heptamolybdate.) The marked stability increase for $[W_4V_2O_{19}]^{4-}$ is evident in its appearance above pH 8, whereas $[Mo_4V_2O_{19}]^{4-}$ only appears below pH 6. It has a higher charge per metal than the decametalate anion, and this is also known to favour W relative to Mo.[19]

One should also not be surprised that V is unable to replace W, in either paratungstate, because to do so would increase the anionic charge unacceptably. The single replacement that can take place at lower pH in the normal diprotio metatungstate, to give **7**, is analogous to the one or two replacements which can occur in the octamolybdate structure, which is the main isopolymolybdate in the same, lower pH range. The single replacement of V for W in metatungstate is not surprising, because the monoprotio metatungstate, which has the same charge, has been identified.[19] The possibility of a second replacement cannot be completely ruled out by our data, although it is not clearly detectable, and no correspondingly charged metatungstate is known.

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