# Molybdotungstovanadates $[V_2Mo_nW_{(4-n)}O_{19}]^{4-}$

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The complete series of hexametalate anions $[V_2Mo_nW_{(4-n)}O_{19}]^{4-}$, with the two vanadiums *cis* and $n$ = 0–4, has been identified in aqueous solution by $^{51}V$ NMR spectroscopy. The vanadium shifts and the p$K_a$ values both increase with increasing substitution of Mo for W. They correlate well with semiquantitative models, showing that somewhat greater changes arise from substitutions taking place in the $V_2O_9$ plane. A consistent preference is also found for like metal atoms to lie mutually *cis*.

The known chemistry and the applications of polyoxometalates are growing rapidly,[1] and yet the rational synthesis of these anions is difficult, because the principles which determine the relative stabilities of alternative structures are as yet unclear. An example of this challenge to structural prediction is provided even by very simple hexametalate anions,[2] having the Lindqvist structure of six $MO_6$ metal–oxygen octahedra, with oxygens edge-shared so as to give an $M_6O_{19}$ double octahedron (Fig. 1). In the case where two of the M atoms are $V^V$ and the other four are $Mo^{VI}$ it has been established that the V atoms strongly prefer a mutually *cis* arrangement, despite apparent electrostatic stabilisation of the alternative *trans* structure.[3] The same holds for the corresponding tungstovanadate,[4] with the *trans*:*cis* ratio being only 1 : 50.[5] A *cis* preference also explains the observed isomers of the $[V_8Mo_2O_{28}]^{4-}$ anion.[6]

In order to investigate this unexpected preference further, and also to obtain quantitative data for the formation constants of polytungstate anions, we have used $^{51}V$ NMR spectroscopy to investigate the entire range of bi- and tri-metallic hexametalate species $[V_2Mo_nW_{(4-n)}O_{19}]^{4-}$, with the two vanadiums *cis* and $n$ = 0–4. The trimetallic species have not previously been studied. These hexametalates dominate the spectra of the aqueous solutions between pH 2.5 and 6, especially as the proportion of W increases. Although they are not all significantly present at any one Mo : W ratio, they can all be obtained as major species by varying this ratio. Their individual $^{51}V$ resonances are narrow (halfwidth *ca.* 30 Hz) even at room temperature, as shown in Fig. 2, a typical spectrum. An exception arises in the spectra of the three anions which lack mirror symmetry in the plane normal to the V–V axis. These resonances are broadened to *ca.* 80 Hz by a $^{51}V$–$^{51}V$ coupling of *ca.* 11 Hz. The various anions are in fairly slow chemical equilibrium, so that their $^{51}V$ resonances are separate apart from accidental overlaps. Therefore, subject to this limitation, and to the unavoidable presence of up to 20% of other metallovanadate anions, they can be fairly reliably integrated. Accidental overlaps can also be partially avoided by obtaining spectra at various pH values. The variation of integral with Mo : W ratio for each resonance then identifies the value of $n$ in the anionic formula above, from the order in which each species reaches its maximum relative integral as the Mo : W ratio is varied. The coupled vanadium resonance pairs were also identified by $^{51}V$–$^{51}V$ correlation spectroscopy (COSY) spectrum[6] at 353 K. The only remaining task of identification is to distinguish the two symmetrical anions having $n$ = 2 (species **4** and **6** below) and to decide which resonance is which for the unsymmetrical anions. This has to be achieved *via* correlations of shift, p$K_a$ *etc.*, validated by the other species.

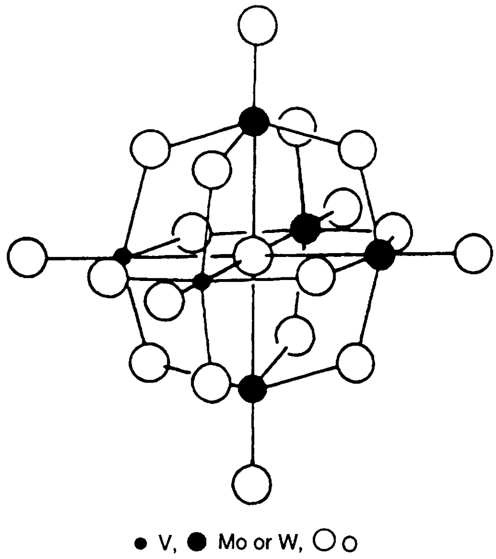

Fig. 1 Lindqvist structure for $[V_2Mo_nW_{(4-n)}O_{19}]^{4-}$

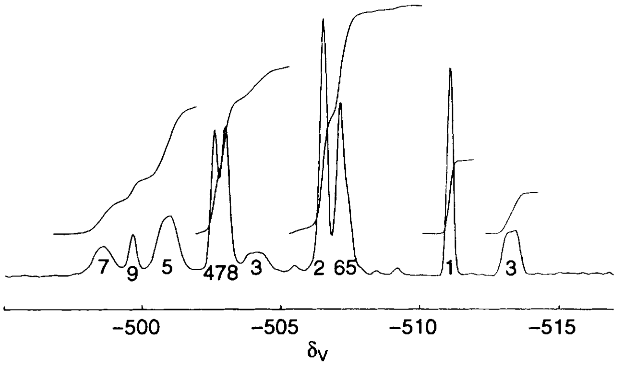

**Fig. 2** A typical spectrum, pH 4.6, 294 K, [W] = [Mo] = [V] = 50 mmol dm$^{-3}$. Peak labels as in Table 1

## Experimental

Solutions were prepared at a sodium concentration of 0.6 mol dm$^{-3}$ from stock solutions of NaCl, $Na_2WO_4$, $Na_2MoO_4$ and $Na_2HVO_4$. Hydrochloric acid was used for acidification. The $^{51}V$ NMR spectra were obtained at 105.2 MHz with a Bruker ACP400 spectrometer, and a pulse-repetition rate of approximately $10T_1$. The solutions were 50 mmol dm$^{-3}$ in V and had varying proportions of Mo and W to give a total

**Table 1** Vanadium-51 chemical shifts and p*K*a values for $[V_2Mo_nW_{(4-n)}O_{19}]^{4-}$ species ($n$ = 0–4)

| Formula | Metal atoms lying in $V_2O_9$ plane | $\delta_V$ for tetraanion | $\delta_V$(est) for monoprotonated tetraanion | p$K_a$(est.) |
|---|---|---|---|---|
| **1** $[V_2W_4O_{19}]^{4-}$ | 2 W | −511.46 | −541 | 1.85 |
| **2** $[V_2MoW_3O_{19}]^{4-}$ | 2 W | −506.80 | −524 | 2.42 |
| **3** $[V_2MoW_3O_{19}]^{4-}$ | W + Mo | −504.3,[a] −513.66 | −525,[a] −527 | 2.42 |
| **4** $[V_2Mo_2W_2O_{19}]^{4-}$ | 2 W | −502.61 | −519 | 2.83 |
| **5** $[V_2Mo_2W_2O_{19}]^{4-}$ | W + Mo | −501.05,[a] −507.38 | −516,[a] −519 | 3.02 |
| **6** $[V_2Mo_2W_2O_{19}]^{4-}$ | 2 Mo | −507.16 | −518 | 3.23 |
| **7** $[V_2Mo_3WO_{19}]^{4-}$ | W + Mo | −498.24,[a] −502.76 | −511, −511[b] | [c] |
| **8** $[V_2Mo_3WO_{19}]^{4-}$ | 2 Mo | −503.08 | −511[b] | 3.31 |
| **9** $[V_2Mo_4O_{19}]^{4-}$ | 2 Mo | −497.94 | −512.5 | 3.74 |

[a] For reasons given in the text, this is believed to be the V nearest to the in-plane Mo. [b] Extrapolated using 353 K data. [c] Not reliably measureable.

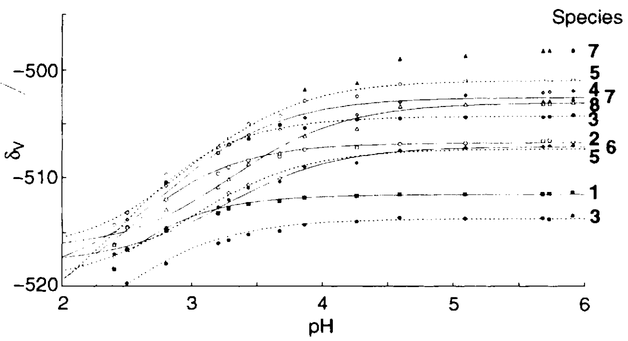

**Fig. 3** Attempted Henderson–Hasselbalch fits of $\delta_V$ *vs.* pH, 294 K. Data (▲) for complex **7** were not fitted in this case because of the weakness of the signals and their overlaps. Data for **9** are in ref. 3. The data points for **5** and **6** overlap above pH 4.5, although the fitted curves are resolved

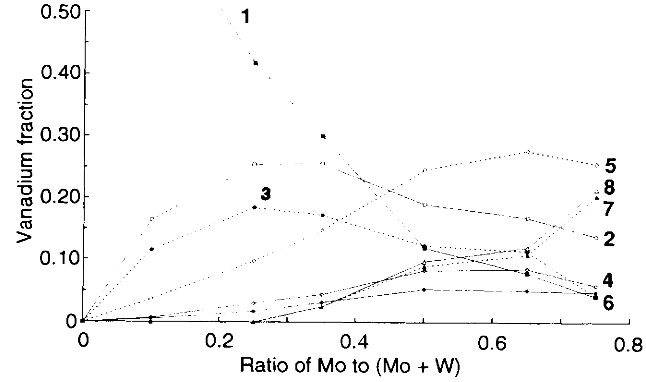

**Fig. 4** Variation with Mo:W ratio of the fraction of each anion measurably present, relative to the total concentration of hexametalate anions. Symbols as Fig. 3 plus ▲, **7**; pH 4.6, 294 K. Line segments serve only to link points

concentration for all three metals of 150 mmol $dm^{-3}$. Although the pH was only measured at 294 K, the spectra of the same solutions were also obtained at 353 K in order to resolve some overlaps of shift, and hence to obtain a more reliable estimate of the relative proportions of the various anions present.

The p$K_a$ values for the various hexametalate anions range from 1.85 to 3.8, and in general these values are little larger than the lower pH limit for stability of the anion concerned. It was therefore difficult to obtain reliable values for either p$K_a$ or for the shifts of the protonated species. Nevertheless, Henderson–Hasselbalch fits to the shift *vs.* pH data were performed, as were the other parameter fits in the Discussion section, using Microsoft EXCEL and SOLVER v.4 (Microsoft Corporation, Redmond, WA, 1992). They gave data showing reasonable trends, and with acceptable agreement of p$K_a$ values when there were two distinct V atoms in the anion. The likely error in p$K_a$ is ±0.3, and ±5 in the shift of the protonated species, although the error for the $V_2W_4$ anion is greater than this. Fig. 3 shows an example of such fits.

## Results

Table 1 lists the shifts and p$K_a$ values obtained at 294 K. A few of the data in this table had to be estimated by extrapolation from the 353 K spectra, which are better resolved, even though their pH values were only measured at 294 K. Previous data[3] were used for the $V_2Mo_4$ anion because this becomes a relatively minor species in the presence of W.

*Integrals.*—Fig. 4 shows the way in which the relative vanadium integrals of anions **1**–**9** vary with Mo:W ratio. In the case of an unsymmetrical anion the two separate integrals have been combined. The errors in integrals can be estimated at ±20% from variations in the data. This plot permits the determination of *n*, in the general formula above, and hence partially justifies the assignments in Table 1. The further assignment of the unsymmetrical species is made by the fact that they show V–V couplings. The remaining uncertainties in assignment are between species **4** and **6**, and between the pairs of resonances of each unsymmetrical species. These are discussed below. Given the **4** *vs.* **6** assignment, we can also compute the integral ratios for the four isomeric pairs which differ only in the mutual exchange of one W for one Mo, namely **2**/**3**, **5**/**4**, **5**/**6** and **8**/**7**. If one divides the ratios **5**:**4** and **5**:**6** by 2 in order to discount the statistical factor inherent in the removal of a symmetry plane, then these average ratios are, in order, 1.50 ± 0.13, 1.80 ± 0.27, 2.21 ± 0.34 and 1.27 ± 0.20:1. The corresponding ratios at 353 K are 1.45 ± 0.08, 1.84 ± 0.50, 2.11 ± 0.41 and 1.23 ± 0.27:1.

## Discussion

*Assignments.*—The first task is to resolve the ambiguities of assignment mentioned above. This may be plausibly achieved by noting how $\delta_V$ for the tetraanion depends on the placement of (say) the Mo atoms. Let us suppose that a substitution of Mo for W in the $V_2O_9$ plane increases the shift of the edge-shared V by 5.60 ppm, but decreases that of the other V by 1.14 ppm. Further that the equivalent substitution of an out-of-plane W increases both vanadium shifts by 4.47 ppm. These shifts were in fact obtained by inspection of the trends in the experimental shifts, followed by least-squares fitting. They give a good prediction for all the vanadium shifts of all the assigned species, and thus effect the remaining assignments also. The correlation of actual and calculated shifts is shown in Fig. 5.

The increase of shift upon substitution of Mo for W matches that found previously in molybdotungstates. One notes that the direct in-plane Mo $\longrightarrow$ V effect of a substitution upon an edge-sharing V (5.60 ppm) algebraically added to the indirect effect

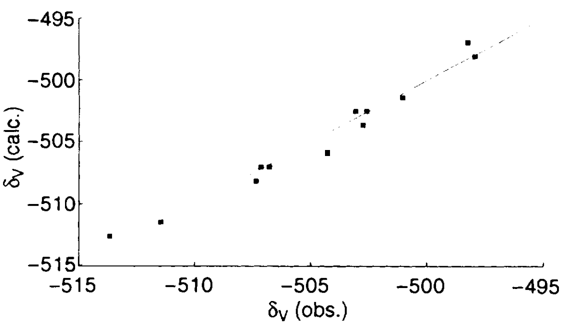

**Fig. 5** Shifts observed for the tetraanion *vs.* shifts calculated as in the text; 294 K. The line represents equality

$\mathrm{Mo} \longrightarrow \mathrm{V} \longrightarrow \mathrm{V}^*$ (−1.14 ppm) is close (4.46 ppm) to the combined direct and indirect effect expected for an out-of-plane substitution, *i.e.* $\mathrm{Mo} \longrightarrow \mathrm{V}$ plus $\mathrm{Mo} \longrightarrow \mathrm{V}^* \longrightarrow \mathrm{V}$ (4.47 ppm observed).

*Protonation.*—One may now seek to understand the variations in p$K_a$ listed in Table 1. Earlier $^{17}$O NMR studies have shown that both the $V_2Mo_4$ and the $V_2W_4$ anions protonate at the edge oxygen between the two V atoms.[3,4] One might therefore anticipate finding a similar relationship between p$K_a$ and the placement of the Mo atoms to that found above for the vanadium shifts, except that it will be simplified by the more symmetrical positioning of the oxygen undergoing protonation. Fig. 6 shows such a relationship. The calculated shifts simply assume an increment in p$K_a$ of +0.58 for every in-plane substitution of Mo for W, and of +0.45 for every out-of-plane substitution. The somewhat greater effect of the in-plane substitution may occur because of greater orbital sharing, through the V atom, between the edge oxygen undergoing protonation and the edge oxygen which is *trans* to it and also bound to an in-plane W or Mo atom. Fig. 6 also adds support to the assignments discussed above.

*Isomer Ratios.*—A full explanation of the observed relative integrals for the isomeric pairs lies beyond present theory. A related study of Mo/W site preferences in the complete series of heptametalate ions $[Mo_nW_{(7-n)}O_{24}]^{6-}$ showed that W had an approximately three-fold preference for the central site, and Mo for the two end sites, each relative to the four corner sites.[7] However, the geometrical difference in the present case between the individual in-plane and the out-of-plane sites is minimal, and indeed the data given above support no simple site-preference model. Instead, one has to ask why, with the $V_2Mo_2W_2$ isomers, there is an approximately two-fold preference for the unsymmetrical isomer **5**, relative to either of the two symmetrical isomers **4** and **6**, but little preference between **4** and **6**.

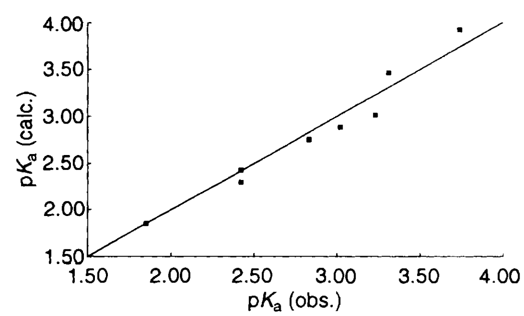

**Fig. 6** Fitted values of p$K_a$ *vs.* values calculated as in the text; 294 K. The line represents equality

Despite this absence of any obvious single-site preference, there is a geometrical difference which can qualitatively explain the isomer ratios given above. In every case, the favoured isomer possesses one more *cis* pair of like metals than does the unfavoured one. Thus **5** has one *cis* V–V pair, one *cis* Mo–Mo pair and one *cis* W–W pair, whereas both **4** and **6** lack one of the latter two pairs. Thus the 50-fold preference for V–V pairing in the $V_2W_4$ anion is paralleled by an approximately 1.7-fold preference for either Mo–Mo or W–W pairing, relative to Mo–W. It is possible that this preference also holds in the heptametalate series,[7] but is obscured by the difficulty of identifying the few species which do not have such *cis*-paired metal atoms, relative to their isomers.

## Conclusion

The bi- and tri-metallic hexametalates can be reliably identified in aqueous solution. They are surprisingly open to empirical predictions of shift, p$K_a$ and isomeric ratios and confirm the earlier conclusion, based on vanadium pairs, that like atoms prefer a mutually *cis* geometry.

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*Received* 27*th April* 1995; *Paper* 5/02689J