Aqueous Molybdotungstates

Ingegärd Andersson,[a] **Jeremy J. Hastings,**[b] **Oliver W. Howarth***[,b] **and Lage Pettersson**[a]
[a] *Department of Inorganic Chemistry, Umeå University, S-901 87 Umeå, Sweden*
[b] *Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*

Molybdenum(VI) has been shown by ^{183}W NMR spectroscopy to replace W^{VI} in the three main types of aqueous polytungstate anion. In ions with the paratungstate-A structure, $[W_7O_{24}]^{6-}$, it can replace any or all of the tungstens, so that at least 19 mixed-metal species can be observed, and mostly also identified. Their relative stability constants can also be approximately determined using the LAKE program. The proportions of these species can be semiquantitatively explained by a simple site-preference model, and their chemical shifts are largely governed by the overall extent of substitution. In contrast, only a single molybdenum substitution was observed in α-metatungstate, α-$[H_2W_{12}O_{40}]^{6-}$, and also in paratungstate-B, $[H_2W_{12}O_{42}]^{10-}$, at the site furthest from the centre of the anion.

There is rapidly growing interest in polyoxometalates, because of new applications such as in selective catalysis and in AIDS therapy.[1,2] These advances are beginning to be underpinned by realistic theoretical calculations.[3] However, the chemistry of polyoxometalates is still far from systematic, because the principles which direct the formation of specific structures are still little understood. One possibility for progress here is to undertake studies in the solution state, so that the thermodynamic stabilities of closely related species may be compared.[4] This paper describes the substitution of Mo^{VI} for W^{VI}, carried out in order to gain a deeper understanding of isopolytungstate and isopolymolybdate structures.

Molybdotungstates have been little studied to date, although Cheetham[5] postulated their existence and also Maksimovskaya *et al.*[6] have described the ^{17}O NMR spectra of some mixed-metal species. Their spectra point to the same heptametalate structure, $[M_7O_{24}]^{6-}$, which is common to both W and Mo. However, so many species are present that it is impossible to identify individual isomers. We here describe a ^{183}W NMR study, where the disadvantage of poor tungsten sensitivity is outweighed by the generous spread of tungsten chemical shifts. This work depends upon earlier investigations of both isopolytungstate and isopolymolybdate chemistry.[7] One broad conclusion is that structures found with only one metal undergo substitution by the other metal only at a single site, but that those known to form with either metal also form with the entire intermediate range of mixed-metal combinations. A second conclusion is that the proportions of the various species are determined much more by the relative preferences of each metal for a given site than by neighbour pairings.

Experimental

Tungsten-183 NMR spectra were obtained at 16.65 MHz as previously described,[7] and at 293 K. The reference shift zero is external 2 mol dm^{-3} aqueous $Na_2[WO_4]$. A few solutions with significant problems of overlap were also studied at 24.98 MHz. The signal-to-noise ratio of all but the weakest peaks was sufficient for at least approximate integration. In fact, several measurements were made at any one metal ratio, and the resulting relative integrals averaged. The error in the measurement of the integrals was typically ±20%. The ratios of species with a given structure depend only weakly upon pH, because metal substitution involves no change of charge. However, independent measurements were performed over the entire range of metal ratios at pH 6.0 and 5.0, and for selected ratios at lower pH. Aqueous solutions were made up by mixing 2 mol dm^{-3} WO_3 (Aldrich) and MoO_3 (AnalaR) dissolved with $LiOH{\cdot}H_2O$ (Aldrich). As the isopolytungstate species, unlike the isopolymolybdates, are known to take several hours to interconvert, all measurements were made on solutions that had had at least 1 d to reach equilibrium. Further checks were made after longer periods; these showed no further changes.

All the anions were present as their lithium salts, and $[Li^+]$ was kept constant in order to fix its known effect upon tungsten shifts. Total metal concentrations were necessarily high, at 2.0 mol dm^{-3}, and so the control of ionic strength had to rely upon self-buffering. This is not a serious constraint in a system with almost constant species charge, and so we were able to carry out calculations of relative equilibrium constants, over a limited range of pH, using the LAKE program.[8] This least-squares computer program is able to treat pH and NMR data simultaneously, and has been found essential for establishing the speciation in highly complex systems such as aqueous molybdovanadates.[4]

Results

Heptametalate Species.—Both W and Mo are known to form heptametalate species $[M_7O_{24}]^{6-}$ in aqueous solution, between pH 7 and 4. Three typical, partial ^{183}W NMR spectra obtained in this pH range, when both metals are present, are shown in Fig. 1. The shift region from δ −50 to −120 corresponds to the four tungsten sites above and below the major symmetry plane of the heptatungstate structure. These are labelled III in Fig. 2(*a*). A further shift region from δ −170 to −190, not shown, corresponds to the outer two in-plane tungstens, labelled II. Similarly, the resonances of the central tungstens, I, fall between δ +240 and +280. These assignments are readily made from peak areas, for the more dominant species such as (0,7) and (1,6) (*i.e.* $[W_7O_{24}]^{6-}$ and $[MoW_6O_{24}]^{6-}$). The shift trends are then evident for other related species. The remaining resonance, B, in Fig. 1 arises from paratungstate-B, $[H_2W_{12}O_{42}]^{10-}$, and is discussed in a later section.

The tungsten resonances were observed to alter in relative area, by groups, as the metal ratio was altered. The order of

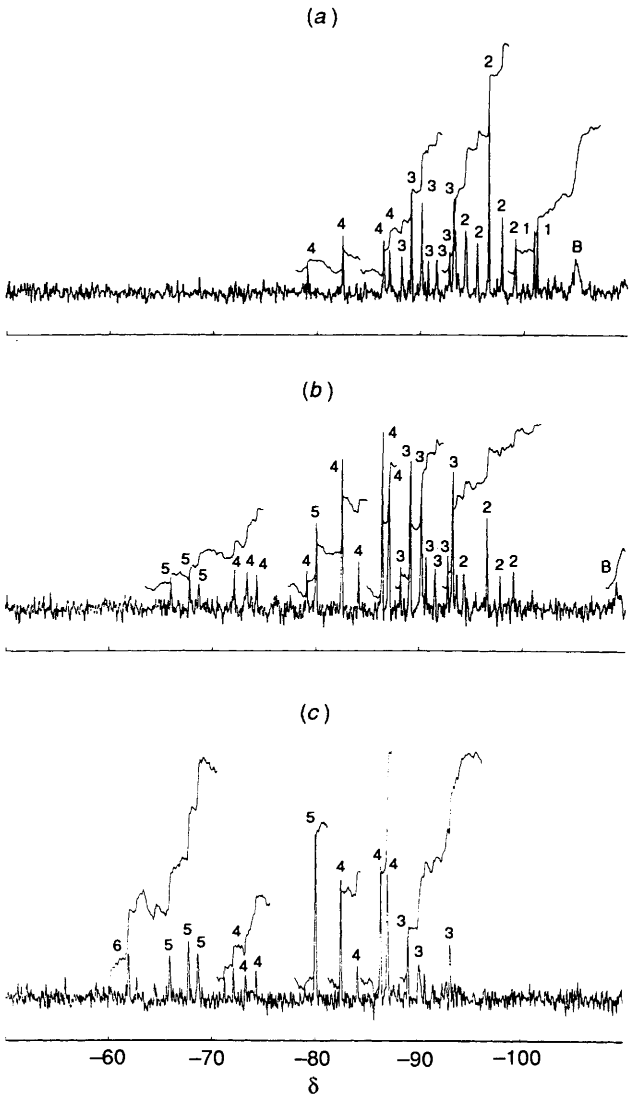

Fig. 1 Typical ^{183}W NMR spectra of mixed-metal heptametalates, showing only the capping (III) tungsten resonance region. All samples were at pH 6, 293 K and 2 mol dm^{-3} total metal. The Mo : W ratios are 2 : 5 (*a*), 1 : 1 (*b*) and 5 : 2 (*c*). The resonances of some species are identified by the number of Mo atoms they contain

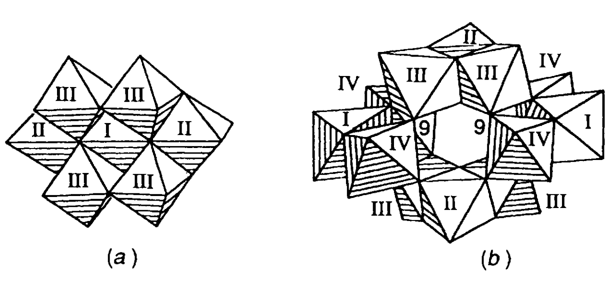

Fig. 2 Structures of (*a*) paratungstate-A, $[W_7O_{24}]^{6-}$, and (*b*) paratungstate-B, $[H_2W_{12}O_{42}]^{10-}$, labelled as in the text

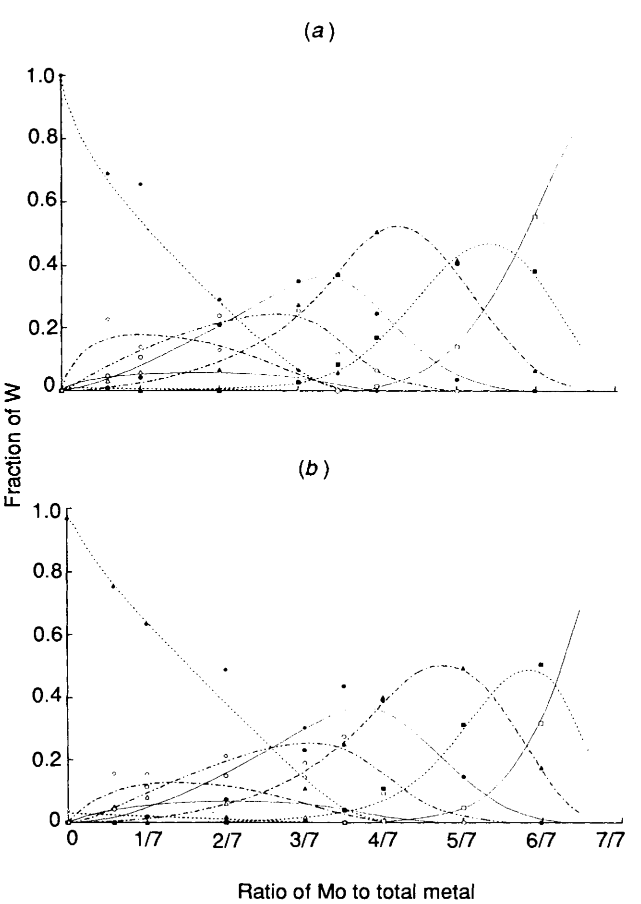

Fig. 3 Dependence of the concentrations of molybdotungstate species, expressed as fractions of total W, upon the total molar [Mo] at [W] + [Mo] = 2 mol dm^{-3}, 293 K, pH 5 (*a*) or 6 (*b*). Experimental plus fitted data: ◆ and ---- (0,12); ◇ and -·-·- (1,11); × and ---- (0,7); △ and ——— (1,6); ○ and -··-··- (2,5); ● and ——— (3,4); ▲ and —·—·— (4,3); ■ and ····· (5,2); □ and ——— (6,1). The lines are output from LAKE[8] after fitting to the same data

dominance of each group reveals the metal ratio within the heptametalate species. Fig. 3 shows how the proportion of each group depends on metal ratio. It also shows the fit obtained when LAKE is used in order to extract equilibrium constants (see below). In most cases, the resonance group could then be subdivided into individual isomers simply by using the necessarily integral ratios of the three tungsten types. The resulting shifts are listed in Table 1. The proposed Greek letter labels follow the convention for the Keggin species, where α represents the highest stability, β the next most stable, *etc.*, once statistical effects have been discounted. It has not yet proved possible to obtain specific site assignments for tungstens of a given type within one isomer, because the signal-to-noise ratio is well below that necessary to see intertungsten couplings. Also, in a few cases the isomer ratios were close to unity, so that these different isomers could not be distinguished either. Nevertheless, twelve species may be identified with reasonable confidence, and others are clearly also present. We may note in passing that many of the mixed-metal anions must be present as racemates.

The ^{95}Mo NMR spectra were also obtained at 89 °C for solutions with several metal ratios. The resonances are quite broad, but may nevertheless be partially resolved into envelopes of overlapping resonances, so as to offer some support for the chemical shift trends discussed below. They are listed in Table 2.

Dodecametalate Species.—The dodecametalate species paratungstate-B, $[H_2W_{12}O_{42}]^{10-}$ forms in almost the same pH range as the heptametalates, but has no molybdenum analogue. It is in slow equilibrium with paratungstate-A, $[W_7O_{24}]^{6-}$,[6,7] and is the major paratungstate under the present experimental conditions. Unlike paratungstate-A, it protonates with pK_a = 4.5. Fig. 4 shows how its shifts vary with pH. Also included are the shifts of six new peaks, the area ratios of which, in falling shift order, are 1 : 2 : 2 : 2 : 2 : 2 (within experimental error) over the entire stability range. These are the only peaks in this range

Table 1 Heptametalates: tungsten shifts and relative amounts of isomers

	Site			Ratio[a]	
Species	I	II	III	observed	statistical
(0,7)	268[b]	−189(2W)	−106(4W)		
α-(1,6)	255	−182	−101(2W), −101.4(2W)	0.67	0.33
β-(1,6)	272	−168, −185	−105, −112, −112.5	0.33	0.67
α-(2,5)	259	None	−96.6(4W)	0.32	0.11
β + γ-(2,5)	258, 243	−162, −185	−94.4, −94.5, −95.2, −92.8, −97.5, −99	0.68	0.89
α-(3,4)	247	None	−89, −90, −93.4	0.67	0.33
β + γ-(3,4)	263, 264	−157, −159	−88.6, −91.0, −92.9, −93.6 [c]	0.33	0.67
α + β + γ-(4,3)	251.0, 252.0, 252.3	None	−83, −86.5, −87.2 (each 2W)	0.76	0.43
δ + ε-(4,3)	267, 268	−136, −139[c]	−72.4, −73.5[c]	0.24	0.57
α-(5,2)	257	None	−80	0.67	0.40
β-(5,2)	None	None	−66	0.33	0.60
γ-(5,2)	None	None	−67.6		
δ-(5,2)	None	None	−69		
α-(6,1)	264	None	None	0.35	0.20
β-(6,1)	None	None	−62	0.65	0.80

[a] Of the listed species only. [b] 1W unless stated otherwise. [c] Other comparable species are also present, with additional resonances which cannot be fully distinguished from these.

Table 2 Shifts and integrals of ^{95}Mo resonances resolvable for heptametalate solutions at 89 °C

Mo : W solution	δ_{Mo}	Linewidth *	Relative integral
All Mo (*i.e.* $[Mo_7O_{24}]^{6-}$)	28.5	320	(1.00)
5:2	21.5	500	0.98
	−9.0	170	0.02
3:4	18.3	580	0.85
	1.8	120	0.09
	−14	140	0.02
	−21	200	0.04
2:5	13.3	330	0.69
	−8.6	290	0.10
	−22.8	360	0.21

* Width at half-height in Hz, after subtraction of broadening due to the window function.

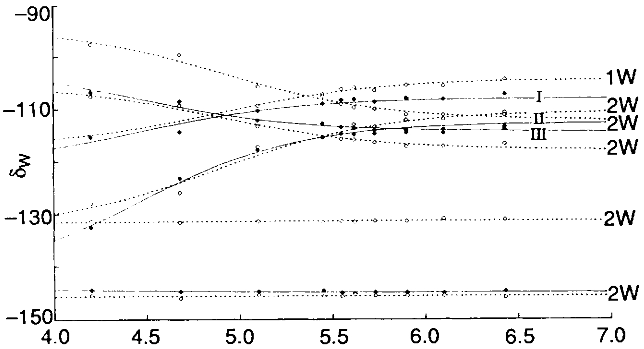

Fig. 4 Tungsten-183 chemical shifts *vs.* pH of the dodecametalates $[H_2W_{12}O_{42}]^{10-}$ [◆, labels as Fig. 2(*b*)] and $[H_2MoW_{11}O_{42}]^{10-}$ (◇) at 293 K

that cannot be attributed either to heptametalates or to $[WO_4]^{2-}$. A typical spectrum covering this shift range is shown in Fig. 5. The new peaks all correspond to the same pK_a of 4.9, *i.e.* 0.4 units higher than that of paratungstate-B. Evidently they arise from the replacement of just one W by Mo in the paratungstate-B structure.

At lower pH, especially around pH 3, tungstate solutions are known[7] to form more compact dodecametalate species, mainly with the α-Keggin structure, such as α-$[H_2W_{12}O_{40}]^{6-}$, whereas molybdate solutions with Li^+ as counter ion[9] form mainly octamolybdate, $[Mo_8O_{26}]^{4-}$. The addition of molybdate to tungstate in this pH range results in the appearance of only one significant new species, the resonances of which were shown elsewhere[10] to be solely consistent with formation of the monosubstituted α-Keggin species $[H_2MoW_{11}O_{40}]^{6-}$.

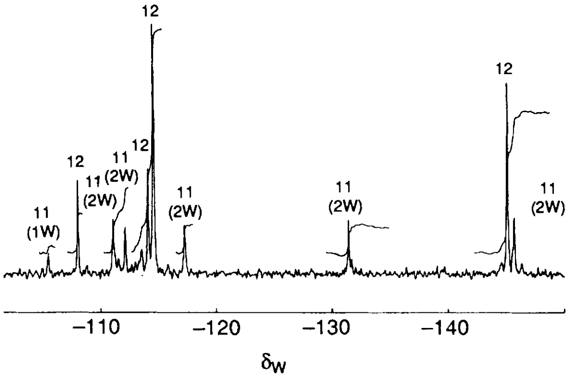

Fig. 5 Tungsten-183 NMR spectrum of $[H_2W_{12}O_{42}]^{10-}$ (12) and $[H_2MoW_{11}O_{42}]^{10-}$ (11) at pH 5.8, 293 K with [W] = 1.43 mol dm^{-3} and [Mo] = 0.57 mol dm^{-3}

Equilibrium Constants.—The present system of species presents unusual problems of definition and of mathematical treatment, for any equilibrium analysis. The $[WO_4]^{2-}$ anion could not be detected in the present solutions. Even $[W_7O_{24}]^{6-}$ appears in one pH 6 solution only, as a minor species in comparison with $[H_2W_{12}O_{42}]^{10-}$. The amounts of mono- and hepta-molybdate also could not be measured quantitatively. Molybdenum-95 NMR spectroscopy is insufficiently sensitive. However, an indirect assessment of molybdenum concentrations for all the molybdotungstate species could be obtained from the tungsten NMR data. The concentration of 'free' Mo was obtained by subtracting this sum from the known total Mo. At pH 6, ['free' Mo] was found to lie between 12 and 57%, and preponderantly at > 40%. At pH 5, however, most Mo was bound in the molybdotungstate anions.

The 'free' molybdate should be present as $[Mo_7O_{24}]^{6-}$ and $[MoO_4]^{2-}$. In the equilibrium calculations, we chose to use

$[Mo_7O_{24}]^{6-}$ and $[W_7O_{24}]^{6-}$ as components. This makes possible a direct comparison of all the possible heptametalate constants. The equilibria are written as in expression (1). This

$$pH^+ + q[Mo_7O_{24}]^{6-} + r[W_7O_{24}]^{6-} \longleftrightarrow (H^+)_p([Mo_7O_{24}]^{6-})_q([W_7O_{24}]^{6-})_r \quad (1)$$

unusual choice of components is feasible because LAKE can treat non-integer values of the stoichiometric constants p, q and r. The species matrix used is shown in Table 3. Preliminary calculations showed that it was essential to allow not only the molybdotungstate formation constants but also that for $[MoO_4]^{2-}$ to co-vary in order to obtain self-consistent constants from the data at both pH values. The fitted curves in Figs. 3(*a*) and 3(*b*) have been calculated from these constants.

Since $[W_7O_{24}]^{6-}$ is only present in very small amounts, and only then at pH 6, the (0,12) constant had to be fixed solely from the pH 6 data. For the same reason, all the constants may be in error by some fixed amount. They also have fairly large errors, which are reflected in the 3σ values in Table 3.

Discussion

Considering the above problems, the fits of the equilibrium constants in Table 3, to the experimental variation of species concentration with metal ratio, shown in Fig. 3, are surprisingly good. The trends shown by these constants are analysed below.

There is also evidence for some site preference from the data for individual isomers in Table 1. Thus, on purely statistical grounds we would expect a ratio of 4 : 1 for the (6,1) species with W in the capping III site (Fig. 2) to the isomeric species with W in the central I site. The experimental value is 2 : 1. Furthermore, we detect no isomer with W at the II site. Similarly, the (1,6) isomers should be in the ratio 4 : 2 : 1 for the single molybdenum substitution at sites III, II and I respectively. In fact, the ratios are approximately 1 : 2 : 0. These ratios are, as expected, independent of pH.

The observed site preferences are all semiquantitatively consistent with a simple site-preference model which assumes that the normalised preference of Mo relative to W for site I (see Fig. 2) is given by the variable x_I, and that corresponding variables x_{II} and x_{III} exist for sites II and III. By normalised, it is meant that the combined effects of the seven substitutions which lead from $[W_7O_{24}]^{6-}$ to $[Mo_7O_{24}]^{6-}$ lead to no net change in the normalised equilibrium constant, so that $x_I \times x_{II}^2 \times x_{III}^4 = 1$. However, the corresponding changes for each intermediate, mixed-metal species will not also be unity, and they will enable the isomeric proportions to be predicted algebraically for a set of species with given metal ratio. For example, the expected concentration ratio for the two main $[MoW_6O_{24}]^{6-}$ species, namely α (one Mo at site II) and β (one Mo at site III) is $(2 \times x_{II})/(4 \times x_{III})$, after due allowance for the number of available sites of either type. The same model also correctly predicts undetectably low abundances for other possible isomers.

The same three variables also predict the ratios of the equilibrium constants, listed in Table 3, because these are also normalised relative to the (0,7) and (7,0) extremes. One obtains the total relative probability for a given metal ratio by summing the relative probabilities for each possible isomer, with appropriate weightings for symmetry-related species. The resulting predictions can then be tested against the data in Tables 1 and 3, and the fit optimised using standard software (Microsoft Excel 4 with Solver). Only one further adjustable parameter is needed at each pH value, namely a fixed scaling multiplier for the mixed-metal constants, presented as logarithms in Table 1, to allow for the probability that the relative values of these constants for the mixed-metal species are considerably more reliable than those for the (low abundance) (0,7) and (7,0) species. The fit is shown in Table 4. Briefly, W prefers a I site (relative to a III site) by a factor of 3.0, and Mo prefers a II site, relative to a III site, by a factor of 4.3. There is no evidence, within the admittedly large experimental error, for any effects from metal substitutions at neighbouring sites.

One can explain these preferences by noting that in the structurally related decavanadate ion $[V_{10}O_{28}]^{6-}$, where the electron density at each atom has been calculated by Bénard and co-workers,[3] this is lowest at the central V atoms. These atoms also have the highest ^{51}V NMR shift, presumably because of the way the shift is dominated by variation of the orbital radius term $\langle r_d^{-3} \rangle$. A low electron density implies

Table 3 Relative log formation constants[a] for molybdotungstate species (Mo,W)

	Species										
	(1,6)	(2,5)	(3,4)	(4,3)	(5,2)	(6,1)	(0,12)	H(0,12)	(1,11)	H(1,11)	(1,0)
p (for H)	0	0	0	0	0	0	0.286	1.286	0.286	1.286	−1.143
q (for Mo)	0.143	0.286	0.429	0.571	0.714	0.857	0	0	0.143	0.143	0.143
r (for W)	0.857	0.714	0.571	0.429	0.286	0.143	1.714	1.714	1.571	1.571	0
log K_{obs} at pH 5 and 6	1.57	2.63	3.14	3.34	2.85	1.88	4.68	9.18[b]	4.73	9.61[b]	−6.07
± 3σ	0.37	0.39	0.44	0.52	0.41	0.61	0.65	(0.65)[c]	0.61	(0.62)[c]	0.15[c]

[a] Relative to (0,7) and (7,0) log $K = 0$. [b] *Via* the pK_a value. [c] Probably an underestimate.

Table 4 Fit of single-site model to pH 6 data

Species (Mo, W)	log K observed*	log K calculated	Isomer ratio	observed	calculated
(0,7)	(0)	(0)			
(1,6)	0.46	1.00	α:β	2.0	2.2
(2,5)	1.52	1.57	α:(β + γ)	0.5	0.5
(3,4)	2.03	1.83	α:(β + γ)	2.0	2.2
(4,3)	2.23	1.83	(α + β + γ):(δ + ε)	3.0	3.2
(5,2)	1.74	1.55	α:(β + γ + δ)	2.0	2.0
(6,1)	0.77	0.98	α:β	0.5	0.7
(7,0)	(0)	(0)			

Calculated site preferences: $x_I = 0.26$, $x_{II} = 3.31$ and $x_{III} = 0.77$. * See text: log *K* for (1,6) to (6,1) decreased by 1.11.

compact d orbitals. We may therefore deduce from the corresponding and well spaced tungsten shifts that the central, I site in the heptametalate structure has the lowest electron density, and also, similarly, that the II site has the highest electron density. Evidently Mo prefers a site with high electron density and W, relatively speaking, one with low. Now W^{VI} is known to form stronger bonds to oxygen than Mo^{VI}.[11] (As an example, this results in lower chemical shifts for O bound to W than for O bound to Mo, at comparable positions in comparable compounds, because of the increase in average excitation energy.) Owing to these stronger bonds, W is less disfavoured by the generally lower availability of oxygen electrons at site I than is Mo. It would therefore appear that the central W atom stabilises the polyanion by resisting the tendency for negative charge to accumulate at its periphery. The behaviour of Mo is the opposite, by default. This analysis receives further confirmation from the W shifts, discussed below.

Since Mo is less able to take electrons from the O atoms surrounding it, these are also therefore more readily protonated. This explains the general observation[7,11] that, in isostructural compounds, the polymolybdates generally have higher pK_a values than those of the polytungstates. The above data for (0,12) and (1,11) confirm this trend in pK_a.

The structure of the monosubstituted paratungstate-B may be deduced with some certainty from the shift data in Fig. 4. The fact that the (0,12) resonances split in the ratio 1:2:2:2:2:2 shows that the substitution has occurred so as to retain an element of symmetry. It must therefore be at either the I or the II site, as labelled in Fig. 2(*b*). Now if we assume that the two species have very similar distributions of charge, then we can anticipate that the set of six tungsten resonances from (1,11) will have shifts and pH dependences rather similar to those of the four tungsten resonances in (0,12). Fig. 4 bears this out. The single-tungsten resonance of (1,11) corresponds to the I resonance of (0,12), and therefore shows that Mo has been substituted at one of these two I sites. Also, the III and IV resonances of (0,12) each split by small amounts into equal halves, as expected. In contrast, the IV resonance splits into one pair of tungsten atoms the shift of which is little affected, plus a second pair with a substantial positive shift, of *ca.* 13 ppm. These must be the two tungstens next to the Mo-substituted I site. Since all the resonances retain dependences upon pH which are very similar to those of (0,12), we may also deduce that the protonation site is unaffected by the substitution of Mo for W. This also supports our contention in an earlier paper[7] that protonation occurs away from the I octahedron, and mainly at O_g.

It is not possible to explain the preference of Mo for a I site in the paratungstate-B structure by any simple extension of the argument from shifts, given above for paratungstate-A. The tungsten shifts of paratungstate-B are far less spread out than those of paratungstate-A, and so do not provide a reliable guide to electron density. Indeed, some of them cross upon acidification. However, one may note that the preferred site for Mo in either structure is that furthest from the anionic centre, which probably means the site with the greatest negative charge.

Shifts.—Table 1 reveals different trends for the shifts of the different types of tungsten atom in the heptametalates as the substitution by Mo increases. Tungstens remaining at positions II and III show a fairly consistent increase of shift with molybdenum substitution, whereas the central tungsten, I, shows rather smaller changes of shift, in the other direction, which correlate very approximately with the asymmetry of its environment. For example, the average shifts of the III (capping) tungstens for the most stable isomer containing them, in the series (0,7), (1,6), *etc.*, through to (6,1), are −106, −101.2, −96.6, −91, −85.6, −80 and −62 ppm respectively. Furthermore, these shifts do not vary much within one isomer, if this has distinguishable III (capping) sites. A similar trend is apparent in the shifts at site II. In contrast, the shifts of the central tungsten I are almost the same in (0,7) as in (6,1), although those in the mixed isomers are up to 21 ppm lower.

We can interpret these shifts as follows. There is some delocalisation through the metal-to-oxygen d_π–p_π bonding network. As a result, the local lowering of bond energy when Mo is substituted for W affects the whole anion, so that the average excitation energy is lessened at all the metal centres. The effect of this is to increase all the tungsten shifts, in approximate proportion to the degree of molybdenum substitution. Also, the increase at a given site is without much positional distinction. However, these influences are partially masked at I, the central tungsten site, by slight gains of negative charge as the surrounding substitutions of Mo for W release electrons.

The ^{95}Mo shift data in Table 2 cannot be assigned to individual species, and indeed must involve some inter-site exchange in Mo-rich anions at this temperature (89 °C). Nevertheless they still clearly show a similar trend, in reverse of course, for the molybdenum shifts. The shifts of each region, where resolved, decrease with increasing tungsten substitution. Thus Table 2 shows the stabilising effects of W in two distinct ways, through shifts and in a reduction of lability.

Rather similar shift trends are apparent when the substituted paratungstate-B (1,11) species is compared with (0,12). Only one of the shifts of the remaining W atoms is significantly decreased (*i.e.* becomes more negative) upon substitution by one Mo. Some of the changes are very small, perhaps because the extent of the delocalisation, as posited above, is somewhat limited in an anion with such a large, open structure. Nevertheless, the trend is clear at all sites except for III. The same is true again when the (1,11) Keggin species is compared with the parent (0,12) anion. Three of the remaining tungstens experience an increased shift, and only one experiences a significant lowering of shift, even though in this case the MO_6 octahedra lie in groups of three, corner-linked by single bridging oxygens rather than edge-linked.

Conclusion

It is somewhat surprising that mixed tungstomolybdates form at all, because the mixed oxides are not known. However, the mixed-metal anions may be able to compensate for any disparities of *e.g.* local charge by positioning the different metals so as to obtain favourable distributions of charge. It is less surprising to find that a structure which is known to occur with only one metal, as an isopolymetalate, resists substitution by the other metal. Indeed, we have no evidence at all for tungsten substitution into $[Mo_8O_{26}]^{4-}$, nor for any other mixed-metal species.

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