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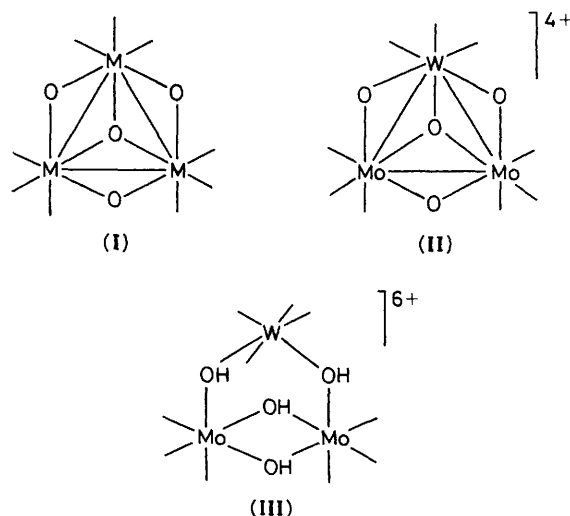
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Reaction of $\text{K}_2[\text{MoCl}_6]$ (or MoCl_4) with $\text{K}_2[\text{WCl}_6]$ in HCl (2 M) at 80°C for 1 h has led to the isolation and characterisation of the first hetero Mo–W trinuclear cluster ‘aqua ion’; $[\text{WMo}_2(\mu_3\text{-O})(\mu_2\text{-O})_3(\text{OH}_2)_9]^{4+}$; subsequent solution studies have shown that both redox properties and water substitution rates at the two molybdenum centres are significantly influenced by the presence of the remote tungsten atom.

The chemistry of triangular cluster ‘aqua ions’ having the incomplete cuboidal structure $[(\text{M}_3)(\mu_3\text{-O})(\mu_2\text{-O})_3(\text{OH}_2)_9]^{4+}$ ($\text{M}_3 = \text{Mo}_3, \text{W}_3$) (I), has been extensively developed.¹ Further detailed studies have involved investigations into the mechanisms governing water ligand replacement reactions.^{2,3} Features of note include a 10^5 difference in water exchange rate at the two different water ligands, with those approximately *trans* to the μ_2 -oxo groups being more labile. In addition these same water sites are responsible for the unusually high acidity (K_a 0.4 M Mo_3 , 0.2 M W_3) of these aqua ion clusters. There is a growing feeling that electronic properties over the entire cluster may be responsible for these reactivity patterns. Such properties are difficult to detect on the homometal species due to the 3-fold symmetry. Recent efforts have thus switched to exploring ways of perturbing the symmetry/reactivity by incorporating heteroatoms in the cluster. Sykes has observed a general increase in the rates of water substitution on replacing systematically all of the μ -oxo groups by sulphido groups.⁴ Our approach has been to investigate the synthesis and properties of heterometal aqua ion clusters of this general M_3X_{13} cluster type and we have prepared a mixed Mo–W derivative on which it is hoped studies may be able to detect influences of a remote heteroatom on the reactivity at a particular site.

Mixed Mo–W species are known in the series of trinuclear bicapped clusters of general formula $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-RCO}_2)_6(\text{OH}_2)_3]^{2+}$ ($\text{M}_3 = \text{Mo}_3, \text{Mo}_2\text{W}, \text{MoW}_2, \text{W}_3$).⁵ We have found that heating 2 : 1 molar quantities of $\text{K}_2[\text{MoCl}_6]$ ⁶ (or MoCl_4)⁷ with $\text{K}_2[\text{WCl}_6]$ ⁸ at 80°C in HCl (2 M) (~ 0.07 M in total metal) for 1 h followed by filtration (removal of blue precipitate),



[†] Taken from A. Patel, Ph.D. Thesis, University of Stirling, December 1988.

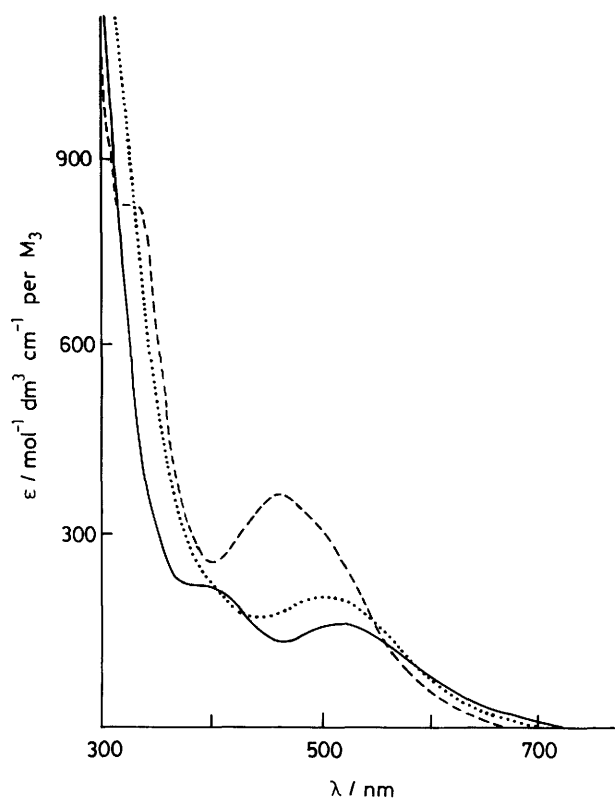


Figure 1. Electronic spectra of trinuclear aqua ions in Hpts solution (2 M): (—) $[\text{WMo}_2\text{O}_4]^{4+}$, (.....) $[\text{Mo}_3\text{O}_4]^{4+}$, (-----) $[\text{W}_3\text{O}_4]^{4+}$.

dilution to 0.5 M H^+ , and DOWEX 50 W \times 2 ion-exchange column chromatography leads to a pinkish-brown band elutable from the column with either toluene-*p*-sulphonic acid (Hpts) (2 M), HCl (2 M), or $\text{CF}_3\text{SO}_3\text{H}$ (2 M).

Flame atomic absorption analysis, using samples of $[\text{Mo}_3\text{O}_4]^{4+}$ and $[\text{W}_3\text{O}_4]^{4+}$ aqua ions as standards, has confirmed the 2:1 ratio of Mo to W in the chromatographically pure pinkish-brown solution. The electronic spectrum of $[\text{WMo}_2\text{O}_4]^{4+}$ (Figure 1) recorded in Hpts (2 M) or $\text{CF}_3\text{SO}_3\text{H}$ (2 M) shows two absorption bands in the visible region at 400 nm ($\epsilon \sim 227$) and 515 nm ($\epsilon \sim 168 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ per WMo_2O_4 unit). These two transitions may be compared to the single transitions observed in the case of $[\text{Mo}_3\text{O}_4]^{4+}$ (505 nm) and $[\text{W}_3\text{O}_4]^{4+}$ (456 nm), and tentatively assigned to arise from the presence of molecular orbitals involved in interactions between both Mo, and Mo and W atoms.

A cyclic voltammogram (Hg cup electrode) recorded in Hpts (2 M) at 25 °C shows one reversible process centred at -0.21 V vs. the normal hydrogen electrode (NHE) prior to the proton reduction limit. Controlled potential electrolysis at -0.3 V generates the electronic spectrum shown in Figure 2(c). The same spectrum can be obtained by titration of $[\text{WMo}_2\text{O}_4]^{4+}$ with two equivalents of Eu^{2+} aqua ion ($E^\circ -0.4 \text{ V}$). Cerium(IV) titration confirmed the formation of the mixed-valence $\text{WMo}_2(\text{III}, \text{III}, \text{IV})$ aqua ion as observed similarly in the case of reduction of both $[\text{Mo}_3\text{O}_4]^{4+}$ (ref. 9) and $[\text{W}_3\text{O}_4]^{4+}$.¹⁰ The electronic spectra of the reversibly formed Mo_3 , W_3 , and now $\text{WMo}_2(\text{III}, \text{III}, \text{IV})$ mixed-valence aqua ions are strikingly similar in profile suggesting a common electronic and molecular structure (III).^{10a,11} The near-IR band at 880 nm ($\epsilon \sim 290$) is similarly assigned to an intervalence transition.^{9,11}

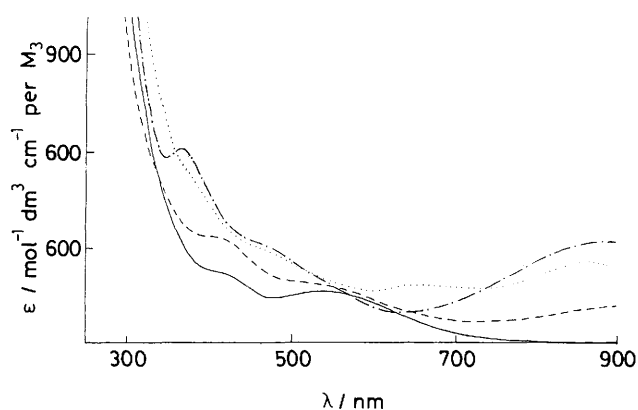


Figure 2. Electronic spectra recorded in Hpts (2 M): (a) (—) $[\text{WMo}_2\text{O}_4]^{4+}$, (b) (-----) + one equivalent of Eu^{2+} , (c) (-.-) + two equivalents of Eu^{2+} , (d) (.....) following treatment with amalgamated zinc.

Titration of $[\text{WMo}_2\text{O}_4]^{4+}$ with one equivalent of Eu^{2+} yields the electronic spectrum in Figure 2(b), which is inconsistent with a 1:1 mixture of $[\text{WMo}_2\text{O}_4]^{4+}$ and $\text{WMo}_2(\text{III}, \text{III}, \text{IV})$ (as observed with both W_3 and Mo_3), and suggestive, in this case, of appreciable formation of the $\text{WMo}_2(\text{III}, \text{IV}, \text{IV})$ intermediate, its existence possibly stemming from the lower symmetry in the electronic structure of this cluster. Further reduction of $\text{WMo}_2(\text{III}, \text{III}, \text{IV})$ can be achieved (with some difficulty) using Zn/Hg (but not Eu^{2+}), giving rise to the spectrum in Figure 2(d) which titrates for an oxidation state of +3 overall. Reduction at the single W atom is believed to be involved here.

A preliminary ^{17}O NMR study (at 40.56 MHz) in Hpts (2 M) carried out on an enriched sample of $[\text{WMo}_2\text{O}_4]^{4+}$ shows resonances (referenced to water) assigned to structure (II) as follows: $\delta +24$ (H_2O opposite $\mu_2\text{-O}$), -14 (H_2O opposite $\mu_3\text{-O}$, Mo and W sites not resolvable), $+800$ [$\text{Mo}-(\mu_2)\text{O-Mo}$], and $+640$ p.p.m. [$\text{Mo}-(\mu_2)\text{O-W}$]. The $\mu_3\text{-O}$ group has not been characterised. ^{95}Mo and ^{183}W NMR studies are in progress.

A kinetic study of the equilibration of NCS^- with $[\text{WMo}_2\text{O}_4]^{4+}$ in $\mu = 2 \text{ M}$ CF_3SO_3^- has been carried out and is consistent with the rate law in equation (1), indicating that initial substitution occurs at the two more labile Mo sites as expected (statistical factor of 2 observed). Forward rate constants (k_f) are approximately 50–60% of those observed on $[\text{Mo}_3\text{O}_4]^{4+}$ in CF_3SO_3^- media with substitution occurring solely through the conjugate-base form (K_a 1.0 M, 25 °C, deprotonation assumed at a Mo H_2O site^{2a}).

$$k_{eq} = k_f[\text{NCS}^-]/2 + k_{aq} \quad (1)$$

The somewhat slower rate constants for NCS^- substitution and the higher acidity constant together with the slightly more negative reduction potential (for reduction presumably at Mo)¹⁰ observed for $[\text{WMo}_2\text{O}_4]^{4+}$ are believed to reflect an electronic influence from the presence of the W atom.^{3c} These findings confirm that the reactivity of a given peripheral water ligand in these clusters is likely to be influenced by the electronic properties of both adjacent and remote metal centres.

Crystalline derivatives: brown-green $(\text{NMe}_4)_5[\text{WMo}_2\text{O}_4(\text{NCS})_9]$ and pink $\text{NaK}[\text{WMo}_2\text{O}_4\{(\text{O}_2\text{CCH}_2)_2\text{NMe}\}_3]$ have been prepared and are being investigated. Full details of the NCS^- kinetic study and of the X-ray crystallography will be reported in a subsequent paper.

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