Reduction of the Incomplete Cuboidal Molybdenum(IV) Aqua Ion $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ by Eu^{2+}. Characterisation of the Trinuclear Molybdenum(III) and Mixed-valence Molybdenum(III,III,IV) Aqua Ions by Oxygen-17 Nuclear Magnetic Resonance Spectroscopy

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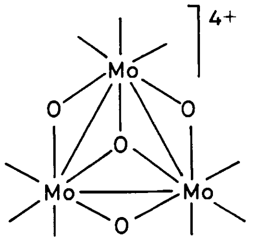
Reduction of ^{17}O-enriched samples of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ by Eu^{2+} in toluene-*p*-sulphonic acid (Hpts) solution has allowed an evaluation of the solution molecular structures of the trinuclear molybdenum(III) and the mixed-valence molybdenum(III,III,IV) reduction products by ^{17}O n.m.r. spectroscopy. An analysis of chemical shifts and peak integrations indicates the structure $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{6+}$ for $Mo^{III,III,IV}$ delocalised on the n.m.r. time-scale at 298 K and two structures $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(OH_2)_9]^{5+}$ (**II**) and $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{5+}$ (**III**) for trinuclear Mo^{III} in an $[H^+]$-dependent equilibrium, (**III**) being favoured at high acidity. Shifts in the energy of the band maximum of $Mo^{III,III,IV}$ at 1 050 nm in media of various dielectric constants together with a successful analysis of the band profile by the method of Hush support its assignment to an intervalence charge-transfer transition. Earlier electrochemical data on $[Mo_3O_4]^{4+}$ and trinuclear Mo^{III} have been re-evaluated with respect to these solution structures. Redox interconversions between the various structures are summarised.

The aqua ion of molybdenum(IV) is now well established as containing the incomplete cuboidal structure $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ (I).[1–4] A number of further studies[5–7] have shown that this ion is readily reduced to a green molybdenum(III) species presumed trinuclear from both the ready reversibility of the redox process and from the fact it possesses a different electronic spectrum from those of the well defined mononuclear[8] and dinuclear[9] aqua ions of Mo^{III}. Oxygen-18[2] and electrochemical[6,7] studies have also shown that the four oxo groups of $[Mo_3O_4]^{4+}$ are retained throughout the redox cycle and become protonated upon reduction suggesting the formula $[Mo_3(OH)_4]^{5+}$ (aq) for the molybdenum(III) product. Extensive protonation consistent with a charge of $>4+$ is also implied from cation-exchange behaviour.[5]

Additional interest has centred on the formation of a mixed-valence molybdenum(III, III, IV) intermediate[5,6] which builds up under certain conditions in equilibrium with the single-valence ions. The position of this equilibrium has been found to depend largely upon the solution acidity[5,6] and nature of the counter anion[7] present, build up of the intermediate being favoured as both the acidity and the co-ordinating tendency of the anion increase. A trend oxalate $> Cl^- >$ pts$^- >$ triflate has been thus established (pts$^-$ = toluene-*p*-sulphonate, triflate = trifluoromethanesulphonate). Electrochemical studies by Paffett and Anson[7] suggest that the less extensive build up of the intermediate in triflic acid solutions may be related to the transfer of only three protons (presumed to the more basic μ-oxygens) during the reduction process. As a result, cyclic voltammograms and polarograms for trinuclear Mo^{III} in triflic acid are less complicated and have enabled detection of two electroactive forms for Mo^{III} with respect to oxidation to Mo^{IV}, the second building up to reach equilibrium with the first over a 30-h period.[7]

Despite these detailed studies, the precise solution structures of these reduction products remain poorly explored. Due to the inherent air sensitivity and delicately balanced equilibria present in these solutions it is clear that a direct definitive solution probe is desirable.

In this paper we report a ^{17}O n.m.r. study of the reduction by Eu^{2+} of ^{17}O-enriched samples of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ in Hpts solution which has enabled an evaluation of the solution structures of the trinuclear molybdenum(III) and mixed-valence molybdenum(III,III,IV) reduction products. The earlier electrochemical and spectrophotometric results have been re-evaluated in respect of the present findings.



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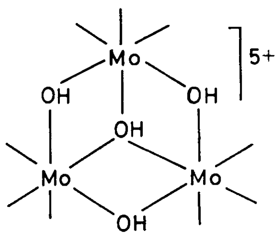

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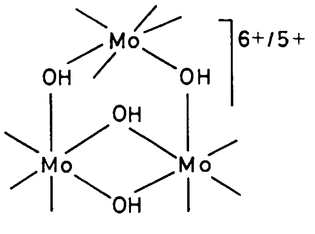

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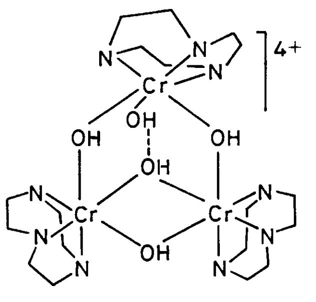

(IV)

Experimental

Preparation of Solutions.—Oxygen-17-enriched samples of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ in Hpts were prepared as de-

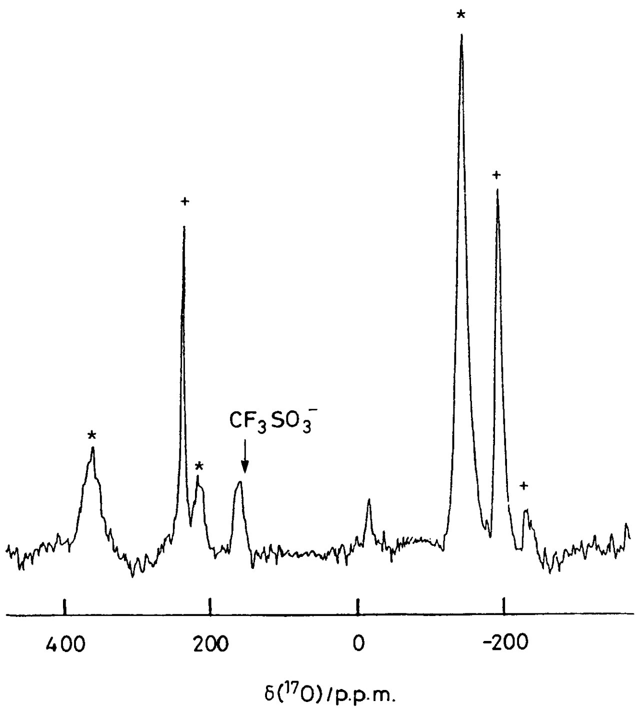

Figure 1. 54.24-MHz ^{17}O N.m.r. spectrum of the trinuclear aqua Mo^{III} ion (0.0096 mol dm^{-3} per Mo_3) generated by reduction with Eu^{2+} of Mo^{IV} in 1.3 mol dm^{-3} Hpts, I = 1.6 mol dm^{-3}, 298 K; Mn^{2+} (0.05 mol dm^{-3}) added. Number of scans = 166 000, sweep width 83 kHz, scanned from +483 to −377 p.p.m. Oxygen-17 enrichments; 3.3 atom % (μ-OH), 4 atom % (bound water). Chemical shifts referenced to $CF_3SO_3^-$ (+159 p.p.m.) and bulk water (0.0 p.p.m.). * Signals due to Mo^{III} structure (**II**); +, signals due to Mo^{III} structure (**III**)

scribed previously[4] to give final μ-oxo and bound water enrichments respectively of 3.3 and 4 atom %. Samples of $H_2{}^{17}O$ were purchased from Yeda Co. Ltd., Rehovot, Israel. Concentrations of $[Mo_3O_4]^{4+}$ were determined at the peak maximum of 505 nm (ε = 189 dm^3 mol^{-1} cm^{-1} in 2 mol dm^{-3} Hpts[6]). The acid Hpts (Sigma) was used as supplied. Triflic acid (Fluka) was purified by distillation under reduced pressure (10 mmHg ≈ 1 330 Pa). The $[H^+]$ of the $[Mo_3O_4]^{4+}$ solutions was adjusted to 1.3 mol dm^{-3} with Hpts and checked by exchange onto a column of Amberlite IR-120 resin (H^+ form). Samples of $Eu(pts)_3{\cdot}9H_2O$ and $Mn(O_3SCF_3)_2{\cdot}6H_2O$ were prepared by dissolution of the oxide (Fluka) and carbonate (BDH) respectively in the appropriate acid and recrystallised twice from water. Solutions of Eu^{2+} in Hpts were prepared by Zn/Hg reduction of solutions of Eu^{3+} under N_2 and standardised with an excess of Fe^{III}/Ce^{IV} using ferroin indicator. Air-sensitive solutions of Eu^{2+} and the reduced molybdenum products were manipulated under N_2 using techniques as described in previous papers.[6,8] Acetonitrile and methanol (May and Baker Pronalys) were used as supplied. Doubly distilled water was used throughout.

N.M.R. Spectroscopy.—The ^{17}O n.m.r. spectra were recorded as 2-cm^3 samples in standard 10-mm tubes on a Bruker AM-400 instrument working at 54.24 MHz at 298 (±0.5) K. Solutions of the molybdenum(III) and molybdenum(III,III,IV) products were generated directly in the n.m.r. tubes by addition of a small volume of 1 mol dm^{-3} Eu^{2+} to the solutions of $[Mo_3O_4]^{4+}$ under N_2 *via* a syringe piercing a septum cap at the top of the tube. Between 30 000 and 200 000 transients, accumulated over total spectral widths of 50—83 kHz as required, were stored and transformed using 1—4 K data points and a pulse width of 12 μs. Chemical shifts were recorded relative to bulk water (0 p.p.m.). Spline functions were added to correct for the rolling baseline due to acoustic ringing. Manganese(II) (1 equivalent per Mo) was added to all solutions to suppress the large bulk water resonance by relaxation[10] and enable monitoring of the bound-water region (±50 p.p.m.). The resonance of the triflate oxygens at natural abundance (0.037 atom%) (159 p.p.m.) served as a convenient internal reference line in the absence of bulk water.

Integrations were performed by paper weighing of the corresponding peak area or by normal Lorentzian peak area analysis.* Uncertainty in the corrections to the rolling baseline limited accuracy of the peak integrations to no better than ±10%. Integrations performed using both methods were in agreement within the quoted errors.

U.v.–visible and visible–near i.r. spectra were recorded on Perkin-Elmer Lambda 5 and Lambda 9 instruments respectively using both 0.1- and 1.0-cm quartz cells at 298 K.

Results and Discussion

Trinuclear Aqua Molybdenum(III) *Ion*.—Addition of 3 equivalents of Eu^{2+} to $[Mo_3O_4]^{4+}$ (final Mo_3 concentration 0.0096 mol dm^{-3}) resulted in the rapid appearance of a deep green solution of trinuclear aqua Mo^{III} with peak maxima [λ/nm (ε/dm^3 mol^{-1} cm^{-1} per Mo_3)] at 635 (240) and 825 (135).[6] A ^{17}O n.m.r. spectrum was then immediately recorded involving 166 000 accumulations over a period of 1 h. During this time simultaneous monitoring of the u.v.–visible spectrum (0.1-cm cell) showed evidence of a small increase in absorbance between 350 and 700 nm similar to that observed by Paffett and Anson[7] over a 30-h period. Here the changes were more or less spontaneous. The resulting ^{17}O n.m.r. spectrum obtained is shown in Figure 1. Two intense resonances at −148 and −197 p.p.m. and a weaker resonance at −228 p.p.m. were assigned to bound water ligands[11] of the molybdenum(III) product, the highly shielded chemical shifts being probably a reflection of the inherent paramagnetism and greater electron density on this ion. The spectrum is as expected completely different from those obtained from both $[Mo_2(\mu\text{-}OH)_2]^{4+}$ (two bound-water resonances at −19 and −42 p.p.m.[4]) and $[Mo(OH_2)_6]^{3+}$ (no bound-water resonances observed[4]) in support of the trinuclear structure. However, in addition there are three resonances attributable to bridging μ-OH groups[4,11] at 355, 232, and 209 p.p.m. clearly not consistent with the presence of a single molybdenum(III) product analogous to that of $[Mo_3O_4]^{4+}$, $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(OH_2)_9]^{5+}$ (**II**). An alternative structure (**III**) $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{5+}$ can also be envisaged involving cleavage of one of the bonds to the μ_3-OH in (**II**) followed by attachment of a further water ligand.

Analysis of the various chemical shifts and peak integrations in Figure 1 has led to assignment to a solution containing 64% (**II**) and 36% (**III**) by the following rationale. Structure (**II**) can be assigned to the following resonances: 355 (μ-OH), 209 (μ_3-OH), and −148 p.p.m. (bound water) on the basis of relative integrations (±10%) of 3:1:9. Structure (**III**) is then assignable to the remining three resonances: 232 (μ-OH), −197 (water opposite μ-OH), and −228 p.p.m. (water opposite water) with respective integrations of 4:8:2 as required. Combining the integrations for each leads to a (**II**):(**III**) ratio of 0.64:0.36. The narrow linewidth of the μ-OH resonance of (**III**) is noteworthy and may be related to a smaller electric field gradient operating for (**III**) in the vicinity of this oxygen.[12] The lack of a

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* Peak area comparison can be made by measurement of the peak width at half height times the height of the peak.

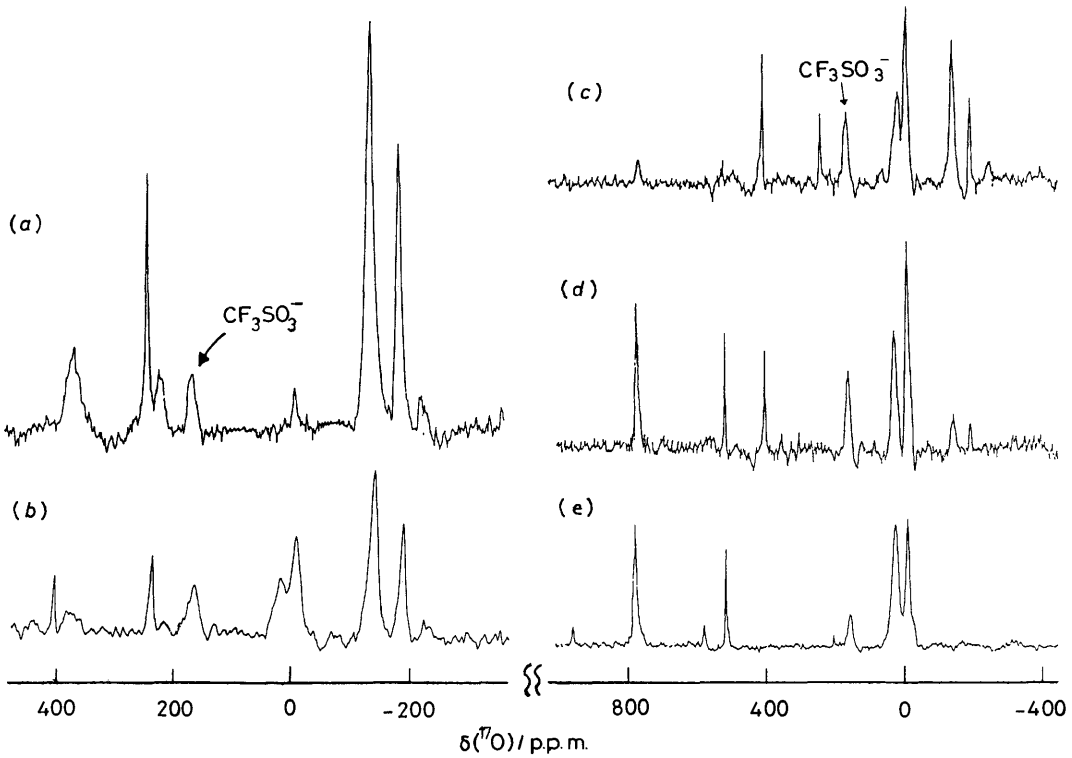

Figure 2. 54.24-MHz ^{17}O N.m.r. spectrum of trinuclear aqua Mo^{III}, conditions as in Figure 1, following successive times of exposure to air: (*a*) 0, (*b*) 10, (*c*) 20, (*d*) 60, and (*e*) 120 min. Sweep width 83 kHz, (*a*) and (*b*) scanned from +483 to −377 p.p.m., (*c*)—(*e*) scanned from +936 to −598 p.p.m.

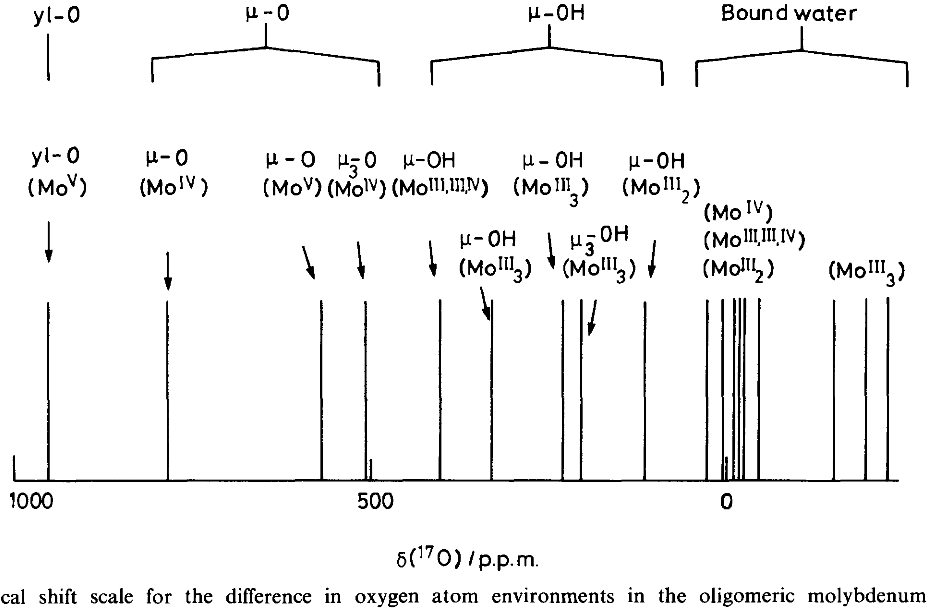

Figure 3. ^{17}O Chemical shift scale for the difference in oxygen atom environments in the oligomeric molybdenum aqua ions in non-complexing acidic aqueous solution. References: $CF_3SO_3^-$ (+159 p.p.m.), bulk water (0.0 p.p.m.)

differentiation between the two expected types of bound water in (**II**) is surprising given the findings for other molybdenum aqua ions[4] but may be related to the large linewidths and paramagnetic properties[7] of this ion.

It is now likely that these structures are responsible for the two electroactive forms of Mo^{III} detected by Anson following zinc reduction of $[Mo_3O_4]^{4+}$ in triflic acid solution,[7] the slow build up of the second form corresponding to conversion of structure (**II**) into (**III**). The much more rapid build up of structure (**III**) in the present study may reflect the use of pts^- rather than triflate, the slightly greater co-ordinating tendency of pts^- possibly promoting cleavage of the Mo–OH(μ_3) bond.

Trinuclear Aqua Molybdenum(III,III,IV) *Ion*.—Air was allowed to diffuse slowly into the n.m.r. tube containing the above mixture of molybdenum(III) products causing spectrophotometric changes consistent with build up of the mixed-valence molybdenum(III,III,IV) intermediate having peak maxima [λ/nm (ε/dm^3 mol^{-1} cm^{-1} per Mo_3)] at 400 (690) and 1 050 (300).[5,6] The present study has allowed monitoring of this redox process

Table 1. ^{17}O Chemical shifts for oligomeric molybdenum aqua ions in non-complexing acid aqueous solution

Oxidation state	Species	Type of oxygen	Chemical[a] shift (p.p.m.)	Integration[b] (per formula unit)	Ref.
+5	$[Mo_2O_4(OH_2)_6]^{2+}$	yl	+964	2.1 ± 0.1	4
		μ-oxo	+582	f1.9 ± 0.1	
		H_2O *trans* to yl	not observed		
		H_2O *trans* to μ-oxo	not observed		
+4	$[Mo_3O_4(OH_2)_9]^{4+}$	μ_3-oxo	+516	1.2 ± 0.2	4 and this work
		μ-oxo	+794	2.9 ± 0.2	
		H_2O *trans* to μ_3-oxo	−7	3.1 ± 0.2	
		H_2O *trans* to μ-oxo	+29	6.2 ± 0.4	
+3.3	$[Mo_3(OH)_4(OH_2)_{10}]^{6+}$	μ-OH	+403	3.7 ± 0.4	This work
		H_2O on bridging Mo	+11	4.3 ± 0.4	
		H_2O on $Mo_2(\mu\text{-}OH)_2$ unit	−13	6.4 ± 0.7	
+3	$[Mo_3(OH)_4(OH_2)_9]^{5+}$ (**II**)	μ_3-OH	+209	1.1 ± 0.1	This work
		μ-OH	+355	2.9 ± 0.3	
		H_2O *trans* to μ-OH	−148	8.6 ± 0.9	
+3	$[Mo_3(OH)_4(OH_2)_{10}]^{5+}$ (**III**)	μ-OH	+232	3.8 ± 0.4	This work
		H_2O *trans* to μ-OH	−197	8.6 ± 0.8	
		H_2O *trans* to H_2O	−228	1.6 ± 0.2	
+3	$[Mo_2(OH)_2(OH_2)_8]^{4+}$	μ-OH	+124	2.2 ± 0.3	4
		H_2O *trans* to μ-OH	−19	3.9 ± 0.4	
		H_2O *trans* to H_2O	−42	4.2 ± 0.3	
	Other signals	$CF_3SO_3^-$	+159	(natural abundance)	

[a] Referenced to bulk water (0.0 p.p.m.). [b] Apparent values per formula unit relative to that of $CF_3SO_3^-$ (0.5 mol dm^{-3}) at natural abundance or bulk water [molybdenum(IV) ion].

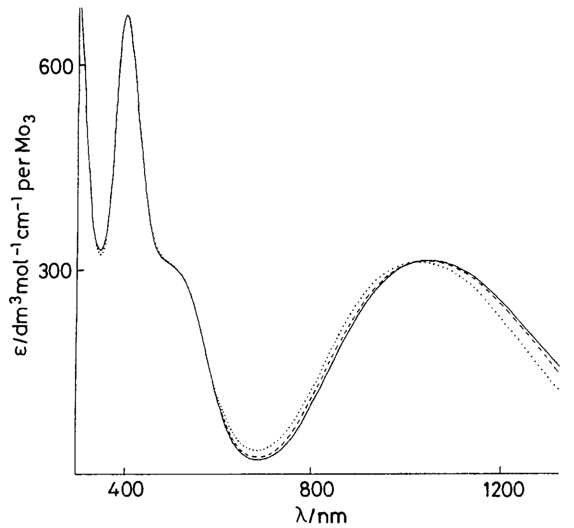

Figure 4. Visible–near i.r. spectra (298 K) for $Mo^{III,III,IV}$ in 3 mol dm^{-3} Hpts diluted 1 in 5 in various media: (——) 3 mol dm^{-3} Hpts, (– – – –) methanol, and (· · · ·) acetonitrile

by ^{17}O n.m.r. spectroscopy directly in the n.m.r. tube as oxidation ultimately to give $[Mo_3O_4]^{4+}$ takes place. Figure 2 shows successive n.m.r. spectra taken at various times following accumulations over a 2-h period by which time regeneration of the original ^{17}O n.m.r. spectrum of $[Mo_3O_4]^{4+}$ had occurred. Maximum build up of the intermediate is apparent in Figure 2(*c*) which contains three new resonances attributable to this diamagnetic[5] species. The two 'broad' resonances at 11 and −13 p.p.m. are assigned to bound water ligands of $Mo^{III,III,IV}$ and the single resonance at 403 p.p.m. to a μ-OH bridging group. The appearance of only one μ-OH resonance is of interest in that it implies a structure analogous to (**III**). Indeed integration of the bound-water and μ-OH regions is consistent with a ratio of 10:4 in support of structure $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{6+}$. Figure 2(*d*) shows clearly the presence of all of the oligomeric molybdenum ions; $[Mo_3O_4]^{4+}$, $[Mo_3(OH)_4]^{5+}$ (both forms), and $[Mo_3(OH)_4]^{6+}$ in equilibrium consistent with the background $[H^+]$ of 1.3 mol dm^{-3}. The present results now allow the evaluation of a chemical shift scale (Figure 3) for oxygen atoms co-ordinated to the various molybdenum aqua ions. Respective chemical shifts and peak integrations of the various oligomeric ions are given in Table 1.

The single μ-OH resonance for $Mo^{III,III,IV}$ is of further interest in that it suggests valence delocalised behaviour on the n.m.r. time-scale. On the other hand the absorption maximum observed at 1 050 nm has been previously assigned[5,6] to an intervalence transition in being uniquely observed for the intermediate in contrast to the single valence ions. Such a transition should therefore be susceptible to a shift in energy in media of varying dielectric constant.[13] Figure 4 shows visible–near i.r. spectra recorded for solutions of $Mo^{III,III,IV}$ in 3 mol dm^{-3} Hpts diluted 1 in 5 with (*a*) 3 mol dm^{-3} Hpts, (*b*) methanol and (*c*) acetonitrile. The shift to higher energy with decreasing dielectric medium from left to right follows the theories of Hush[14] and Hopfield[15] and confirms the intervalence charge-transfer nature of the transition. Furthermore the band profile has been subjected to an analysis by the method of Hush[14] for weakly interacting mixed-valence species. In such cases a relationship (1) should exist between the Gaussian band width

$$\Delta\bar{\nu}_{max.} = 47.9\,(\bar{\nu}_{max.})^{\frac{1}{2}}\ (\bar{\nu}\text{ in cm}^{-1}) \qquad (1)$$

at half height $\Delta\bar{\nu}_{max.}$ and the band energy $\bar{\nu}_{max.}$. Secondly the degree of delocalisation (α) can be estimated from equation (2)

$$\alpha = (4.2 \times 10^{-4}\varepsilon_{max.}\Delta\bar{\nu}_{max.}/\bar{\nu}_{max.}d^2)^{\frac{1}{2}} \qquad (2)$$

where d = the interatomic distance involved (assumed to be 260 pm*). Finally, the electronic exchange energy resulting

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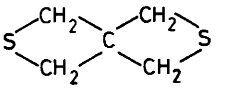
* 260 pm is a reasonable estimate for the Mo^{III}–Mo^{IV} distance in $Mo^{III,III,IV}$ (aq), being slightly longer than the known[3] Mo-Mo distance (248 pm) in $[Mo_3O_4(OH_2)_9]^{4+}$ and close to the value (255 pm) found in the only crystallographically characterised molybdenum(III,III,IV) complex $[Mo_3OCl_3(O_2CCH_3)_3(OH_2)_3]^{2+}$ (A. Bino, Z. Dori, and F. A. Cotton, *Inorg. Chim. Acta*, 1979, **33**, L133).

Table 2. Parameters representing a number of Class IIA mixed-valence transition-metal ions according to the theory of Hush[14]

Complex[a]	Intervalence band (cm^{-1}) $\bar{\nu}_{max.}$	$\Delta\bar{\nu}_{max.}$ (obs.)	$\Delta\bar{\nu}_{max.}$ (calc.)	$10^2\alpha$	E_{ex}[b] (cm^{-1})	Ref.
$[(bipy)_2ClRu^{III}(dppe)Ru^{II}Cl(bipy)_2]^{3+}$	8 020	4 600	4 300	1.14	92	16
$[(NH_3)_5Ru^{III}LRu^{II}(NH_3)_5]^{5+}$[c]	10 989	6 600	5 040	2.45	269	17
$[(bipy)_2ClRu^{III}(pyz)Ru^{II}Cl(bipy)_2]^{3+}$	7 900			4.47	353	18
$Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 14H_2O$	14 100			4.0	564	19
$[(NH_3)_5Ru^{III}(pyz)Ru^{II}(bipy)_2Cl]^{4+}$	10 400			5.48	569	20
$[Mo_3(OH)_4]^{6+}$ (aq)	9 524	4 600	4 680	9.49	903	This work

[a] dppe = $Ph_2PCH_2CH_2PPh_2$, bipy = 2,2′-bipyridyl, pyz = pyrazine. [b] E_{ex} (electron exchange energy) is calculated from first order perturbation theory to be $\alpha\nu_{max.}$(cm^{-1}). [c] L =



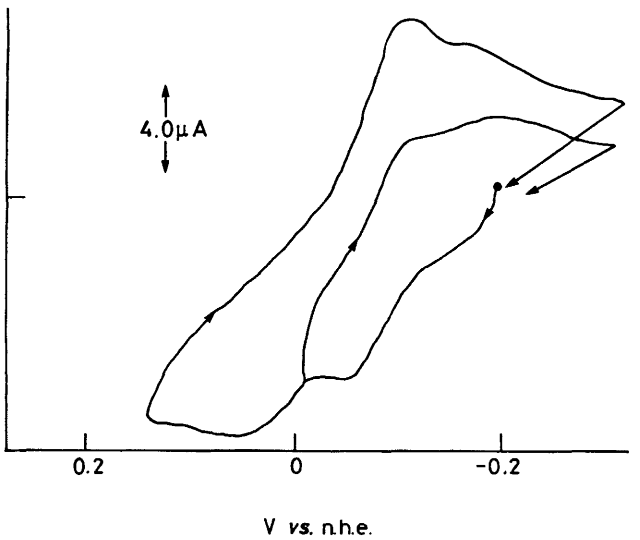
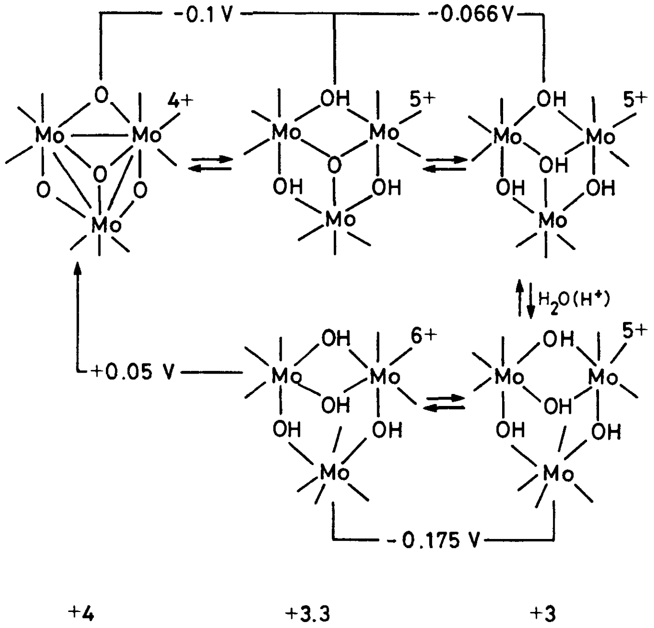


Figure 5. Cyclic voltammogram from a solution of trinuclear aqua Mo^{III} (5.0 mmol dm^{-3}) generated in 2.0 mol dm^{-3} Hpts under argon at 298 K. Electrode: hanging mercury drop; scan rate 0.1 V s^{-1} [taken from Figure 5(*c*) of ref. 6]

from the intervalence transition (E_{ex}) can be evaluated from first-order perturbation theory as equal to $\alpha\bar{\nu}_{max.}$ (cm^{-1}). It is found that the intervalence band profile stands up well to the above analysis with excellent agreement resulting between calculated (4 680 cm^{-1}) and experimental (4 600 cm^{-1}) $\Delta\bar{\nu}_{max.}$ values in further support of the intervalence assignment. Furthermore the values of α (9.49×10^{-2}) and E_{ex} (903 cm^{-1}) compare well with those obtained from a number of well defined weakly interacting mixed-valence complexes[16–20] (Table 2). It is thus concluded that on the electronic time-scale the molybdenum(III,III,IV) representation is correct whereas rapid chemical and thus electronic equivalence of the molybdenum centres appears to be relevant to the slower n.m.r. time-scale at 298 K.* Similar findings are apparent from studies on the analogous tungsten(III,III,IV) ion which possesses an intervalence transition at 678 nm[21] but equivalent μ-OH groups (at 252 p.p.m.) in the ^{17}O n.m.r. spectrum.[22]



Scheme. Interconversion between trinuclear aqua ions of molybdenum-(III) and -(IV); 2.0 mol dm^{-3} Hpts, 298 K

The Electrochemistry of Trinuclear Aqua Molybdenum(III) *Revisited*.—The present findings now allow a re-evaluation of the previous results from cyclic voltammetric studies on trinuclear Mo^{III} in Hpts solution. Figure 5 shows the cyclic voltammogram obtained[6] for 5 mmol dm^{-3} Mo^{III}_3 in 2 mol dm^{-3} Hpts solution. Three oxidation waves are observed for the molybdenum(III) product involved with oxidation to give ultimately $[Mo_3O_4]^{4+}$. The reversible process centred at −0.175 V (*vs.* n.h.e.) is now assigned on the basis of it being the most negative potential to the couple $[Mo_3(\mu\text{-}OH)_4]^{6+/5+}$ both having structure (**III**). Structure (**II**) for Mo^{III} might on the other hand be capable of being readily oxidised back to $[Mo_3O_4]^{4+}$ without requiring build up of the intermediate (mismatch of structures). The second oxidation wave at −0.042 V is thus assigned to this three-electron oxidation process and is coupled with a reduction wave at −0.09 V observed on the return scan. Corresponding solutions of $[Mo_3O_4]^{4+}$ show a reduction process occurring at −0.1 V believed now to be due to the reverse of this process [formation of (**II**)]. Finally, the irreversible oxidation wave at +0.05 V is only observed in reduced solutions where appreciable amounts of Mo^{III,III,IV} are

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* Experiments aimed at an estimation of the thermal barrier to electronic/chemical exchange in the molybdenum(III,III,IV) ion by variable-temperature ^{17}O n.m.r. studies (< 0 °C) in aqueous methanol solution are planned for the future.

present and is thus assigned to oxidation of structure (**III**) to $[Mo_3O_4]^{4+}$ (mismatch of structures). Thus build up of the mixed-valence intermediate is explained as follows. As the acidity of the molybdenum(IV) solution increases structure (**III**) for the molybdenum(III) product becomes favoured *via* acid-catalysed cleavage of a Mo–OH(μ_3) bond. This then leads to a favourable outer-sphere cross redox reaction with $[Mo_3O_4]^{4+}$ as oxidant resulting in build up of the intermediate, the degree of comproportionation relating as discussed previously[6] to the difference between the most positive $[Mo_3O_4]^{4+}$ reduction potential and the most negative molybdenum(III) oxidation potential here due to the couple $[Mo_3(\mu\text{-}OH)_4]^{6+/5+}$ involving structure (**III**). The interconversions between the various oligomeric aqua ions of Mo discussed in this paper are summarised in the Scheme.

A specific anion effect with respect to build up of the intermediate has also been noted (oxalate > Cl^- > pts^- > triflate). Such behaviour appears to relate to changes in the redox potential differences[6,7] described above and may relate to the ability of the anion effectively to neutralise the high positive charge on the intermediate by ion association or in the case of oxalate by co-ordination. However some inner-sphere role in promoting the cross redox reaction cannot also be ruled out.

Finally, structure (**III**) is not unprecedented in the literature. A chromium(III) complex $[Cr_3(\mu\text{-}OH)_4L_3(OH)]^{4+}$ (**IV**) (L = 1,4,7-triazacyclononane) has been crystallographically characterised.[23] A trinuclear aqua ion is known for Cr^{III} which is assumed to have structure (**II**)[24] although there appears no evidence at present which can rule out a contribution from structure (**III**).

In conclusion the present ^{17}O n.m.r. study has allowed an evaluation of the solution structures for the molybdenum-(III) and -(III,III,IV) products obtained following reduction by Eu^{2+} of $[Mo_3O_4]^{4+}$ in Hpts solution. A structure $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{6+}$ delocalised on the n.m.r. time-scale is relevant for $Mo^{III,III,IV}$ whose band maximum at 1 050 nm has been unequivocally assigned to an intervalence transition. Two structures $[Mo_3(\mu_3\text{-}OH)(\mu\text{-}OH)_3(OH_2)_9]^{5+}$ (64%) and $[Mo_3(\mu\text{-}OH)_4(OH_2)_{10}]^{5+}$ (36%) are relevant for solutions of trinuclear Mo^{III} generated in 1.3 mol dm^{-3} Hpts. Build up of the intermediate under conditions of high acidity and co-ordinating ability of the counter ion has been correlated with formation of structure (**III**) for Mo^{III} leading to favoured comproportionation with $[Mo_3O_4]^{4+}$ with further stabilisation of the intermediate effected by charge neutralisation.

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