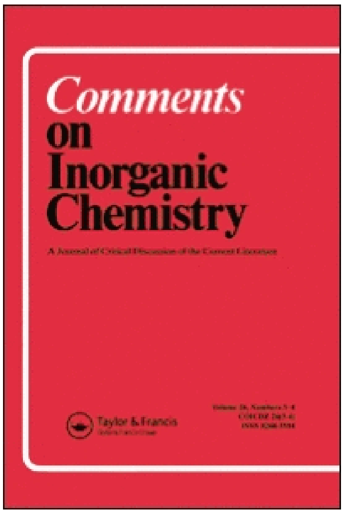

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The Aquo Ions of Molybdenum

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To cite this Article Richens, David T. and Sykes, A. Geoffrey(1981) 'The Aquo Ions of Molybdenum', Comments on Inorganic Chemistry, 1: 3, 141 — 153

To link to this Article: DOI: 10.1080/02603598108078087

URL: http://dx.doi.org/10.1080/02603598108078087

The Aquo Ions of Molybdenum

Recent extensive research into the aqueous solution chemistry of molybdenum has led to the preparation and characterization of aquo ions in oxidation states (II) through (VI). It is appropriate at this time to report on the area and comment on the diversity of chemistry exhibited by these ions.

Whereas the complexities of Mo(VI) aqueous solution chemistry have been understood in general terms for some time, it is only in the last 15 years that aquo ions of the lower oxidation states have been identified, Table I, and their structures established. Aquo ions have a somewhat elevated importance, since they are often regarded as a point of reference or prototype of the behavior expected of an oxidation state. So far as detailed structures are concerned, metal aquo ions are notoriously difficult to crystallize for x-ray diffraction studies. Structures of derivative complexes can and have been determined however, and, by using a range of physicochemical techniques, these can be related with some certainty to the aquo ions.

TABLE I
Single oxidation state aquo ions of molybdenum

Oxidation state	Description	Formula	Color
Mo(II)	Dimer	$[Mo_2(H_2O)_8]^{4+}$	Red
Mo(III)	Monomer	$[Mo(H_2O)_6]^{3+}$	Pale yellow
	Dimer	$[Mo_2(OH)_2(H_2O)_8]^{4+}$ or $[Mo_2O(H_2O)_{10}]^{4+}$	Green
	Trimer		Green
Mo(IV)	Trimer	$[Mo_3O_4(H_2O)_9]^{4+}$	Red
Mo(V)	Dimer	$[Mo_2O_4(H_2O)_6]^{2+}$	Yellow
Mo(VI)	Monomer ($pH > 7$)	$[MoO_4]^{2-}$	Colorless
	Polymers ($pH < 7$)	$[Mo_7O_{24}]^{6-}/[Mo_8O_{26}]^{4-}$	Colorless
	Monomer/Dimers ($pH < 1$)		Colorless

Comments Inorg. Chem.
1981, Vol. 1, pp. 141–153
0260–3594/81/0103–0141/$06.50/0

Molybdenum(VI) is without question the most stable oxidation state. It is only the mildest of oxidants, in contrast to its congenor Cr(VI). All other aquo ions, including the V state, are oxidized in air to give eventually Mo(VI). Oxidation states II and III require anaerobic techniques (N_2 or Ar gas, syringes, Teflon tubing, and/or stainless steel needles, rubber seals), and the IV and V states have to be stored under air-free conditions, although air oxidation is not extensive over limited ≈1-hour periods. Perchlorate ions cannot be used with the II and III state ions, and appear also to oxidize (although in a somewhat random and unpredictable manner) the IV state. Instead non-complexing, redox inactive, and strongly acidic *p*-toluenesulphonic acid, $C_6H_4(CH_3)(SO_3H)$ (abbreviated to HPTS), or trifluoromethanesulphonic acid, CF_3SO_3H (abbreviated to HFMS), are used as a source of hydrogen ions.

Three Mo compounds are available as "lead ins" for the chemistry described. These are sodium molybdate(VI), $Na_2[MoO_4]\cdot 2H_2O$, and molybdenum hexacarbonyl $[Mo(CO)_6]$,[1] (both widely available), and potassium hexachloromolybdate(III), $K_3[MoCl_6]$. The latter is prepared by electrolytic reduction of $[MoO_4]^{2-}$ in concentrated HCl followed by the addition of KCl.[2]

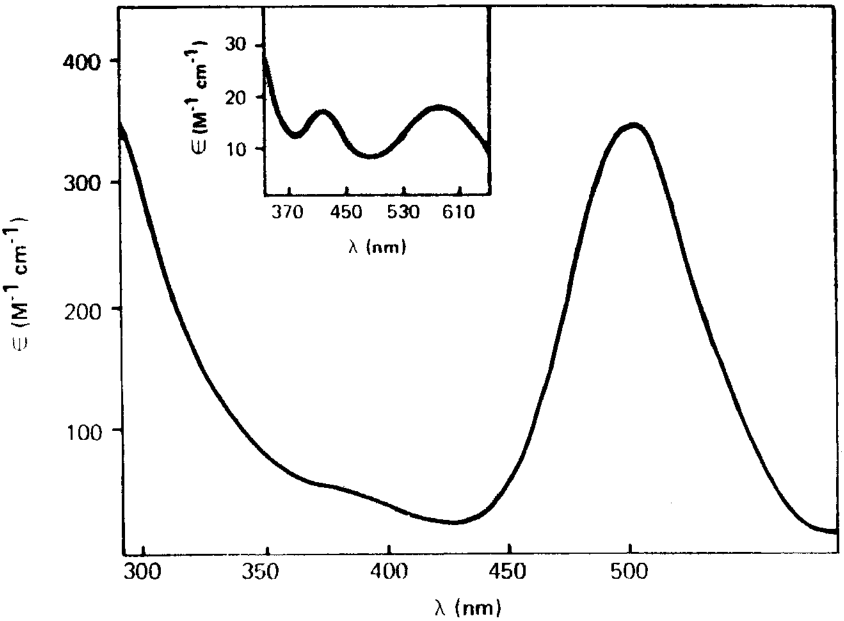
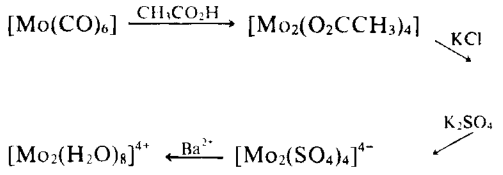


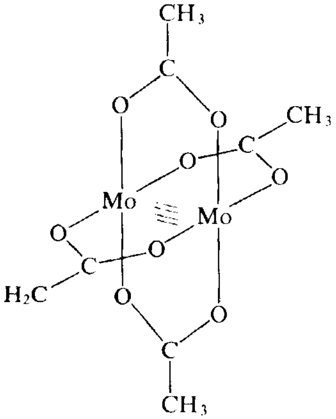
FIGURE 1 uv-visible spectra (ε's per dimer) of the Mo(II) dimer, $[Mo_2(H_2O)_8]^{4+}$, $[H^+] = 1.0$ M using HFMS. The inset is the spectrum of the Mo(II, III) complex in 1 M H_2SO_4.

Significant contributions to the isolation of II and III state ions have been made by Bowen and Taube.[3] The red dimeric aquo Mo(II) ion, spectrum in Figure 1, is prepared from $[Mo(CO)_6]$ by a route as in (1):



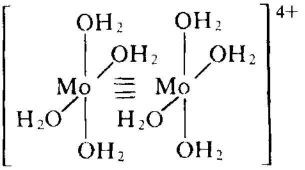
(1)

Both the acetato complex (A) (bridging ligands) and chloro complex (no bridging ligands) are examples of complexes having quadruple metal–metal bonds, a subject to which Cotton and colleagues have recently devoted much attention[4]:



(A)

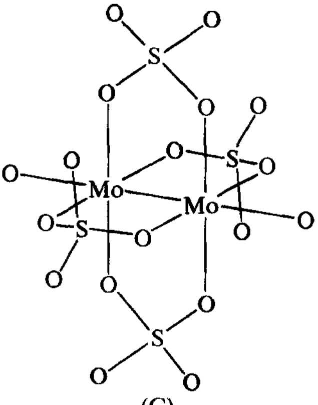
The cationic charge of the Mo(II) aquo ion was found to be >3. A comparison of the visible spectrum in 1 M H^+ with that of $[Mo_2Cl_8]^{4-}$ in 6 M HCl, and $[Mo_2(en)_4]^{4+}$ (en = ethylenediamine; bridging by en is unlikely) suggests that the multiple metal–metal bond is retained in the $Mo(II)_2$ aquo ion, and that the structure is $[Mo_2(H_2O)_8]^{4+}$, (B), here abbreviated to Mo_2^{4+}:



(B)

Water molecules weakly coordinated in the axial positions are not ruled out. In acidic solutions Mo_2^{4+} can be kept for long periods of time in the absence of O_2.

When pink $K_4[Mo_2(SO_4)_4]\cdot 2H_2O$ is recrystallized from 1 M H_2SO_4 in the presence of traces of O_2, red-blue crystals of the Mo(II,III) complex $K_3[Mo(SO_4)_4]\cdot 2.5H_2O$ are obtained.[5] This complex is paramagnetic ($\mu_{eff} = 1.65$ B.M.) and has been characterized by EPR spectroscopy. Structures of $[Mo_2(SO_4)_4]^{4-}$ (the axial oxygen is from an adjacent sulfate) and $[Mo_2(SO_4)_4]^{3-}$ (the axial oxygen is an H_2O) are very similar:



(C)

with the Mo-Mo distances 2.11 and 2.16 Å, respectively.[6] A half-wave potential of 0.47 V (vs NHE) has been determined for the $[Mo_2(SO_4)_4]^{4-/3-}$

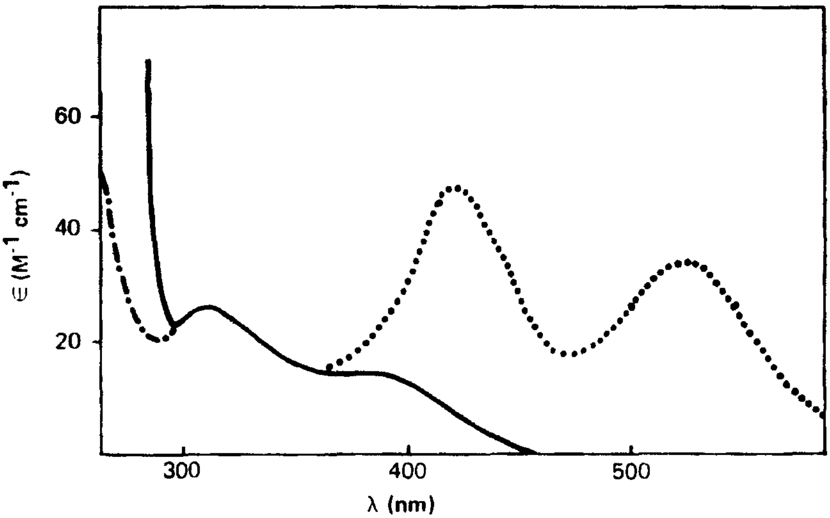
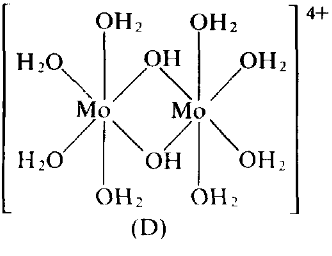


FIGURE 2 uv-visible spectra of $Mo(H_2O)_6^{3+}$, $[H^+] = 1.0$ M using HPTS (——) and HBF_4 (•—•), and $MoCl_6^{3-}$ (•••) in 12 M HCl.

couple. One-electron oxidation products of $[Mo_2(O_2CC_3H_7)_4]$ and $[Mo_2X_8]^{4-}$ ($X^- = Cl^-, Br^-$) have also been reported. The Mo(II,III) sulfato complex gives a blue solution in 2 M H_2SO_4, inset to Figure 1.[7] Under these conditions $[Mo_2(SO_4)_4]^{3-}$ or a partly aquated sulfato complex is present. Attempts to prepare the Mo_2^{5+} aquo ion by addition of strong acids (HCl or HPTS) to solid $K_3[Mo_2(SO_4)_4]\cdot 2.5H_2O$ result in disproportionation to give a red solution of Mo_2^{4+} and a molybdenum (III) species. Quantitative re-formation of the blue color is observed on addition of H_2SO_4. Air oxidation of the blue Mo(II,III) solutions is reported to give $Mo(IV)_3$. The different structure types involved in these interconversions makes this chemistry of considerable interest.

Bowen and Taube[8] also reported air-free aquation (2 days) of $[MoCl_6]^{3-}$ followed by Dowex cation-exchange resin separation, as a procedure for the preparation of the pale yellow, III state aquo ion. Traces of O_2 can result in contamination with the yellow Mo(V) ion, $Mo_2O_4^{2+}$, which can obscure the d–d bands in the uv spectrum,[9] Figure 2. A comparison of the spectrum with that of $[MoCl_6]^{3-}$ (structure established as monomeric and octahedral) strongly suggests that the ion is hexaaquo. At present $[Mo(H_2O)_6]^{3+}$ is the only monomeric and paramagnetic (3.69 B.M.) aquo ion. Interestingly, $[Mo(H_2O)_6]^{3+}$ is more labile than $[Cr(H_2O)_6]^{3+}$ by a factor of $\sim 10^5$ in the 1 : 1 reaction with thiocyanate.[10] This is explained by the increased associative character of the reaction of $[Mo(H_2O)_6]^{3+}$. Pathways involving the conjugate-base $[Mo(H_2O)_5OH]^{2+}$ make little or no contribution, alongside the dominant associative path involving $[Mo(H_2O)_6]^{3+}$.

A green Mo(III) product is obtained on reduction of Mo(VI) as molybdate, or Mo(V) as $Mo_2O_4^{2+}$ in acid solution ($[H^+]$ generally 0.5–2.0 M).[11] The reduction can be achieved using a Zn/Hg Jones reductor column, or by electrolytic reduction at a Hg pool electrode at −0.5 V (vs NHE). The product is purified on a Dowex cation-exchange resin column. The charge per Mo was found to be ~2 and the elution behavior indicated a total charge of 4+.[11] From earlier studies by Hartmann and Schmidt[12] it had been incorrectly supposed that this ion was $[Mo(H_2O)_6]^{3+}$. It is not certain whether the structure is di-μ-hydroxo, formula $[Mo_2(OH)_2(H_2O)_8]^{4+}$, or μ-oxo, formula $[Mo_2O(H_2O)_{10}]^{4+}$:



(D)

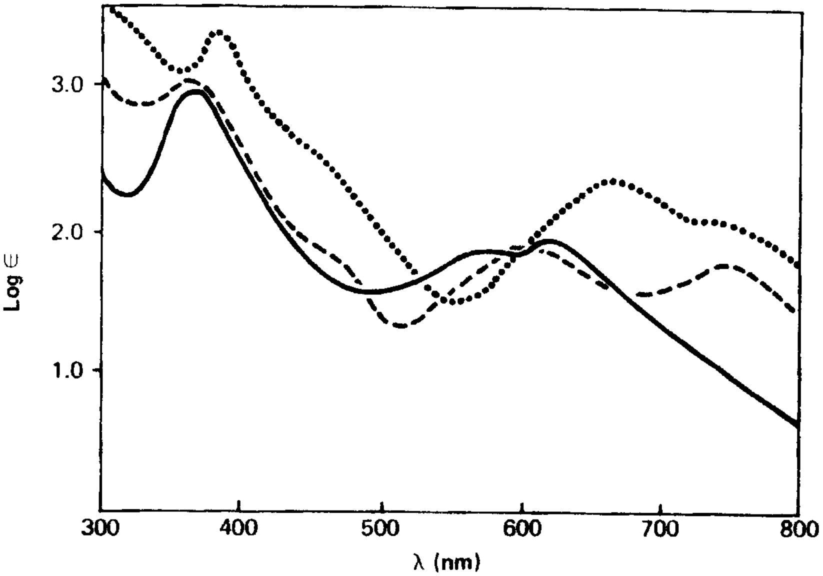
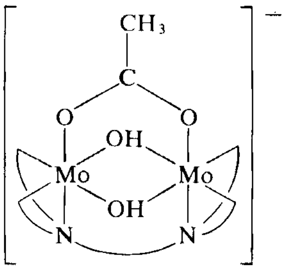


FIGURE 3 uv-visible spectra (ε's per dimer) for the Mo(III) aquo dimer (——), $[H^+] = 1.0$ M using HPTS, and the $Mo(III)_2$–edta complexes $[Mo(III)_2(OH)_2(O_2CCH_3)(edta)]^-$ (D) (– – –), and $[Mo(III)_2(OH)_2(NCS)_2(edta)]^{2-}$ (· · ·) at pH 6.

An x-ray crystal structure of the $Mo(III)_2$-edta complex ion (edta = ethylenediaminetetraacetate), prepared by reduction of the $Mo(V)_2$-edta complex in acetate buffer, has been determined[13]:



(E)

The similarity of the spectrum to that of the $Mo(III)_2$ aquo ion, Figure 3, suggests (but no more) that a di-μ-hydroxo structure applies.

Souchay and colleagues were the first to identify a red Mo(IV) aquo ion, Figure 4.[14] The procedure involves heating molybdate(VI) (from Na_2MoO_4) or the Mo(V) aquo ion $Mo_2O_4^{2+}$ with Mo(III) (generally $[MoCl_6]^{3-}$) in 2 M H^+ for ≈1–2 hours at 80–90°.[15] The product is allowed to aquate and the

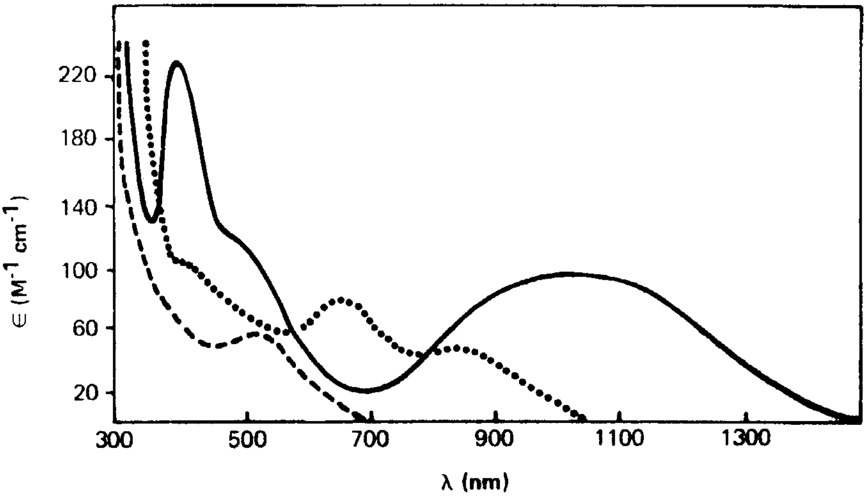
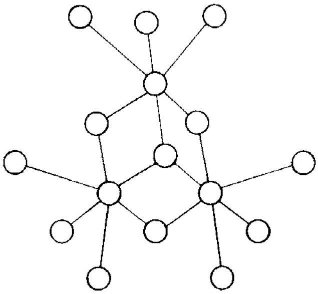


FIGURE 4 uv–visible spectra (ε's per Mo) for the Mo(IV) aquo trimer, $[Mo_3O_4(H_2O)_9]^{4+}$, (——), the Mo(III) aquo trimer (···), and the mixed oxidation state trimer Mo(III, III, IV) (——).

final purification is again performed using ion-exchange methods. X-ray crystal structures of the oxalato, $Cs_2[Mo_3O_4(C_2O_4)_3(H_2O)_3]\cdot 4H_2O$,[16] and thiocyanato $[(CH_3)_4N]_4[Mo_3O_4(NCS)_8(H_2O)]$ complexes,[17] prepared from the Mo(IV) aquo ion, indicate trinuclear structures. The very elegant ^{18}O labelling experiments by Murmann and Shelton[18] have confirmed that the Mo_3O_4 unit is retained in solution. The experiments carried out included dissolving the labelled thiocyanato complex in H_2O (Hg^{2+} was added to induce dissociation of NCS^-), and then converting the aquo ion back into $[Mo_3O_4(NCS)_8(H_2O)]^{4-}$, a cycle which was achieved with <2% exchange. It is concluded that the aquo ion is $[Mo_3O_4(H_2O)_9]^{4+}$:



(F)

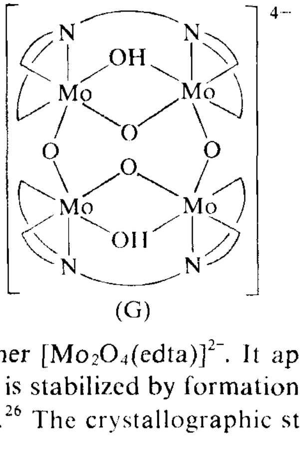
Previously from cryoscopic,[19] electrochemical,[20] and kinetic studies,[21] it had been incorrectly deduced that dimeric or monomeric structures applied.

While studies using EXAFS[22] rule out a monomer, they do not allow a choice to be made between dimeric and trimeric structures. Participation of statistically related equivalent sites in a trimer is a likely explanation of the kinetic behavior.

It is of interest that the oxidations of $[Mo(H_2O)_6]^{3+}$ and aquo $Mo(III)_2$ with one-equivalent oxidants $[Co(C_2O_4)_3]^{3-}$ and $[IrCl_6]^{2-}$ proceed through to the Mo(V) aquo dimer, $Mo_2O_4^{2+}$, even when there is a deficiency of oxidant.[23] It is concluded here that intermediate Mo(IV) species are of a highly reactive and transient nature. Only the trimeric aquo ion appears to be stable. The high temperature required for its formation suggests that a high kinetic barrier may be involved.

Reduction of $Mo(IV)_3$ on a Zn/Hg Jones reductor yields a green species which titrates for Mo(III).[24] The spectrum, Figure 4, is significantly different from that for the Mo(III) dimer. Air re-oxidation as well as electrochemical reversibility strongly suggest that the trimeric core structure is retained. The electrochemical studies have also led to the spectrophotometric identification of a Mo(III,III,IV) aquo ion, Figure 4, the formation of which is more favorable at the higher $[H^+]$ values. At $[H^+] = 0.5$ M there is a 30% yield, at $[H^+] = 2.0$ M 80%, and essentially quantitative formation at $[H^+] > 4.0$ M. The sensitivity to $[H^+]$ clearly implicates protonation effects in these interconversions. A feature of the spectrum is a broad intervalence band at 1050 nm. Further characterization of the $Mo(III)_3$ and Mo(III, III, IV) aquo ions in terms of net charge (ion-exchange chromatography) as well as crystal structures of related complexes is required. No Mo(III, IV, IV) intermediate has been detected.

Azide ion oxidation of the $Mo(III)_2$–edta complex, $[Mo_2(OH)_2(O_2CCH_3)edta]^-$, (E), yields an intensely red colored tetrameric mixed Mo(III, III, IV, IV) oxidation state complex,[25] $[Mo_4O_4(OH)_2(edta)_2]^{4-}$



(G)

along with the Mo(V) dimer $[Mo_2O_4(edta)]^{2-}$. It appears that the Mo(III, IV) dimer initially formed is stabilized by formation of the tetramer or undergoes further oxidation.[26] The crystallographic study was crucial in the

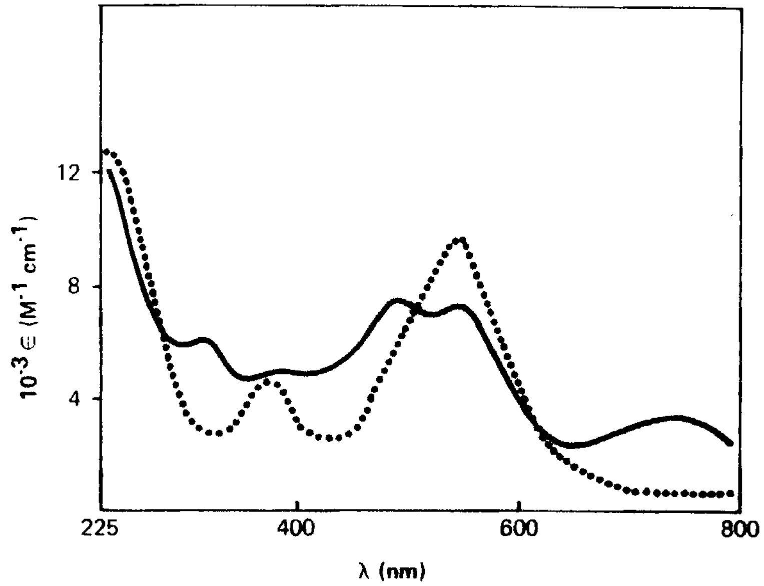
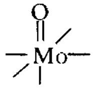


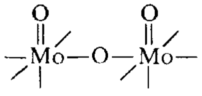
FIGURE 5 uv–visible spectra (ε's per tetramer) for the Mo(III, III, IV, IV)–edta complex, $[Mo_4O_4(OH)_2(edta)_2]^{4-}$ (——) and the $Mo(IV)_4$–edta complex $[Mo_4O_6(edta)_2]^{4-}$ (···) in H_2O.

characterization of this complex.[25] Features are the symmetry of the complex with four identical Mo sites and hydroxo as well as oxo bridges. Controlled air oxidation yields a $Mo(IV)_4$–edta complex, $Mo_4O_6(edta)_2^{4-}$, Figure 5. No analogous tetrameric aquo ions have yet been prepared, and it may well be that the edta ligand is essential to the formation and retention of such structures.

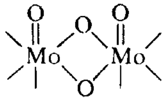
There are three Mo(V) structure types[27]



(H)

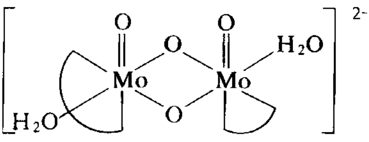


(I)

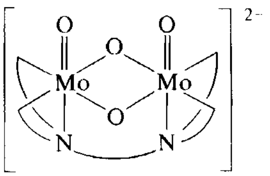


(J)

where thiocyanate appears unique in giving all three: $[MoO(NCS)_5]^{2-}$, $[Mo_2O_3(NCS)_8]^{4-}$, and $[Mo_2O_4(NCS)_6]^{4-}$. Possibly the best known monomeric form is the green chloro complex $(NH_4)_2[MoOCl_5]$ which is retained in >7 M HCl. Dilution of such solutions leads to formation of (J). The linear structure [I] can give rise to *cis* (as shown) or *trans* rotamers (with respect to the terminal oxo ligands). Linear structures are fairly common, a good example being dithiocarbamates which can be isolated from nonaqueous solvents, e.g., $[Mo_2O_3(S_2COEt)_4]$. It is interesting to speculate whether an aquo ion $Mo_2O_3^{4+}$ might be prepared. One suspects not, but a special stability (and inertness) of the Mo–O–Mo unit might just result in some detectable (if transient) species being generated. The third Mo(V) structure, type (J), is dominant so far as the aqueous solution chemistry is concerned. Reduction of acidified molybdate(VI) by N_2H_4 followed by ion exchange, or by controlled potential reduction at a mercury-pool electrode, $[Mo(VI)] < 10$ mM in 2 M $HClO_4$ at potentials between -0.05 and 0.15 V(vs NHE), proceeds smoothly to yield orange–yellow solutions. On the basis of ion-exchange and cryoscopic measurements, Ardon and Pernick[28] demonstrated that the ion is dimeric and of charge 2+. The $Mo_2O_4^{2+}$ core structure is known to be present in a wide range of complexes, e.g., $[Mo_2O_4(C_2O_4)_2(H_2O)_2]^{2-}$ (K), and the complex $[Mo_2O_4(edta)]^{2-}$, (L):

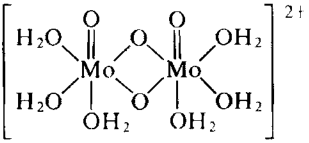


(K)



(L)

Spectra have similar features, see Figure 6. Once formed the ion



(M)

is stable over a wide $[H^+]$ range, 0.01–6 M $HClO_4$, but in less acidic solutions (pH > 2) hydrolysis leading to precipitation of $MoO(OH)_3$ occurs. A stable polymeric Mo(V) species, spectrum (in H_2O) as shown in Figure 6, can be obtained from Mo(V) solutions at pH 6.[30] On addition of 0.1–0.5 M $HClO_4$, $Mo_2O_4^{2+}$ is obtained.

The $Mo_2O_4^{2+}$ ion is diamagnetic, indicating spin pairing between the d^1 Mo(V) centers. The short Mo–Mo distance (~2.5 Å) suggests metal–metal bonding or superexchange via the oxo bridges.

When H_2S is passed through a solution of $[Mo_2O_4(cysteine)_2]^{2-}$ the two μ-oxo ligands, and (surprisingly) not the terminal oxo's, are replaced by μ-sulfido groups.[31] Addition of 5 M $HClO_4$ results in aquation of the cysteines with the formation of the $Mo_2O_2S_2^{2+}$ aquo ion. The $Mo_2S_4^{2+}$ core is known to form in some instances when P_4S_{10} is used.[32] A feature of the $Mo_2O_4^{2+}$ ion is the high substitution lability of the aquo ligands *trans* to the terminal oxo group (as with VO^{2+}). This is a direct consequence of the dis-

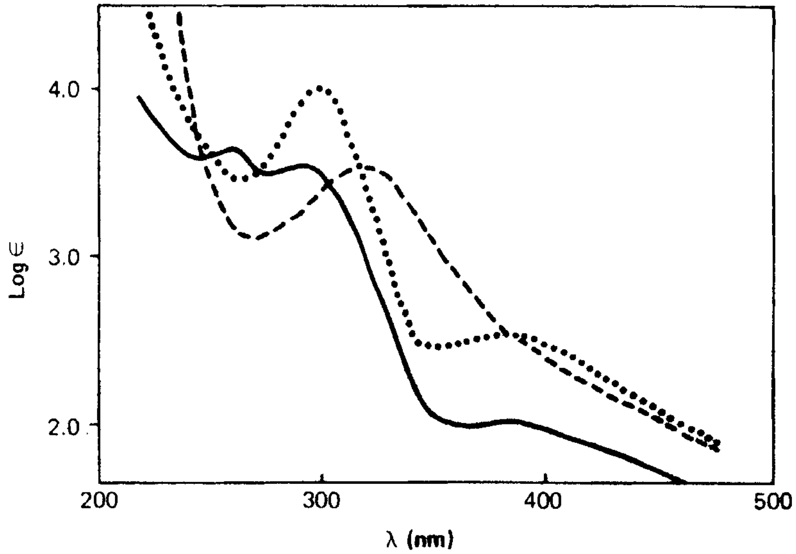


FIGURE 6 uv–visible spectra for the Mo(V) aquo dimer, $[Mo_2O_4(H_2O)_6]^{2+}$, $[H^+] = 0.5$ M using $HClO_4$ (——), the related dimer $[Mo_2O_4(edta)]^{2-}$ (···) at pH 5 (acetate buffer), and for polymeric Mo(V) (---). Molar absorptivities (ε) are per dimer for the first two complexes, and per Mo for the third.

placement of the Mo(V)'s from the plane of the complex towards the terminal oxo ligands. Occupancy of an equatorial coordination position is thermodynamically more favorable. Substitution is still rapid and well into the stopped-flow range.[33,34]

Oxidation of $[Mo_2O_4]^{2+}$ with $[IrCl_6]^{2-}$ or $[Fe(phen)_3]^{3+}$ has resulted in the identification of competing pathways.[35] The first, an oxidant-independent pathway, is the result of dimer undergoing change to a modified form $*Mo(V)_2$, or to monomeric species,

$$Mo(V)_2 \longrightarrow 2Mo(V) \tag{2}$$

which then reacts rapidly with oxidant. Direct attack of oxidant on the dimer also occurs. No evidence was obtained for formation of a Mo(V,VI) intermediate, which is presumably short-lived. However, when the complex (L) is used with $[IrCl_6]^{2-}$ or $[Fe(phen)_3]^{3+}$ as oxidant, the reverse of the first step in the scheme (3)–(5) is seen to contribute

$$Mo(V)_2 + Ir(IV) \rightleftharpoons Mo(V,VI) + Ir(III), \tag{3}$$

$$Mo(V,VI) \longrightarrow Mo(V) + Mo(VI), \tag{4}$$

$$Mo(V) + Ir(IV) \longrightarrow Mo(VI) + Ir(III), \tag{5}$$

and addition of $[IrCl_6]^{3-}$ drastically decreases the rate of the reaction.[36]

At pH > 7 molybdenum(VI) is present as molybdate, $[MoO_4]^{2-}$. Exchange with $H_2{}^{18}O$ is slow at pH > 10 and first-order rate constants (k_{obs}) conform to the dependence[37]

$$k_{obs} = a + b[OH^-]. \tag{6}$$

On decreasing the pH, exchange becomes faster due to the high reactivity of protonated $[MoO_4]^{2-}$ [38]:

$$[MoO_4]^{2-} + H^+ \rightleftharpoons [MoO_3(OH)]^- \quad (K = 10^{3.7}). \tag{7}$$

Protonation also has the effect of inducing a change in coordination number[39]:

$$[MoO_3(OH)]^- + H^+ + 2H_2O \rightleftharpoons [Mo(OH)_6] \quad (K = 10^{3.7}) \tag{8}$$

At pH < 7 sufficient quantities of $Mo(OH)_6$ are generated to induce polymerization to octahedral Mo_7 and Mo_8 species, which are present as $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$. There are no detectable amounts of polynuclear species between Mo_1 and Mo_7 in solution. In the solid state Mo_2, Mo_4 and Mo_6 forms are known, and structures of these and other polymolybdates are considered in more detail elsewhere.[40] Of these $[Mo_2O_7]^{2-}$, prepared by addition of $[(n\text{-}Bu)_4N]^+OH^-$ to acetonitrile solutions of $(n\text{-}Bu_4N]_4[Mo_8O_{26}]$, is a new species.[41] The dimer has a tetrahedral structure similar to dichromate and retains its structure in organic solvents even when water is added. On addition of smaller cations (Na^+ and Me_4N^+) it reverts to $[Mo_7O_{24}]^{6-}$. Monomeric and dimeric Mo(VI) aquo ions are present in equilibrium at $[H^+] > 0.2$ M and octahedral coordination seems likely. The dimerization of monomeric Mo(VI) has been investigated spectrophotometrically in perchloric acid solutions $[H^+] = 0.5$–3.0 M, I = 3.0 M.[42] Three dimeric species have been suggested. At $[H^+] > 6$ M other evidence suggests that there is formation of MoO_2^{2+}.[43]

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