Preparation and Properties of New Molybdenum–Ethylenediaminetetra-acetato-complexes formed by the Oxidation of the Molybdenum(III,III) Dimer $[Mo_2(O_2CMe)(OH)_2(edta)]^-$

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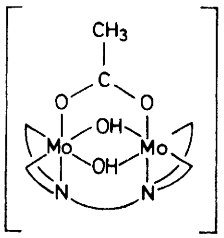
Oxidation of the molybdenum(III,III) dimer μ-acetato-μ-ethylenediaminetetra-acetato(4−)*NN′OO′O″O‴*-di-μ-hydroxodimolybdate(III), $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, by the two-equivalent oxidant N_3^- yields a cyclic molybdenum(III,IV) mixed oxidation state tetramer, and the already well characterized molybdenum(V,V) dimer $[Mo_2O_4(edta)]^{2-}$. It has been demonstrated that displacement of acetate and co-ordination of azide, as well as acid dissociation of one of the hydroxo-bridges (pK_a 7.73), precede oxidation. The ratio of products (up to 37% tetramer) can be accounted for by formation of an intermediate, possibly a $Mo^{IV,IV}$ dimer, for which the two initial reactants, the $Mo^{III,III}$ complex and N_3^-, compete. Controlled oxidation of a solution of the $Mo^{III,IV}$ tetramer with O_2 yields the analogous $Mo^{IV,IV}$ tetramer which has also been isolated. The reduction potential of the two tetramers has been determined in aqueous solution, pH 7.43, and is +0.07 V. Both tetramers react readily with oxidants, *e.g.* $[Co(NH_3)_5Cl]^{2+}$ ($t_{\frac{1}{2}}$ <1 min). Oxidation of the $Mo^{III,III}$ dimer with Mo^V and Mo^{VI} complexes, $[Mo_2O_4(edta)]^{2-}$ (on heating) and $[Mo_2O_6(edta)]^{4-}$ respectively, yields a polymeric molybdenum(IV) species.

THE starting complex in the studies reported herein is the molybdenum(III,III) dimer, $K[Mo_2(O_2CMe)(OH)_2(edta)]$,[1] the structure of which has been reported.[2]



The reactivity of the analogous complex in which the μ-acetato-group is replaced by two N-bonded thiocyanates [3] has also been studied. The principal oxidant investigated is the azide ion N_3^-. Other oxidants include the di-μ-oxo-molybdenum(V,V) complex $[Mo_2O_4(edta)]^{2-}$, and the molybdenum(VI,VI) complex $[Mo_2O_6(edta)]^{4-}$ in which the edta, tridentate at each molybdenum, spans two MoO_3 centres. At the outset the aim was to prepare a dimeric $Mo^{IV,IV}$ species, which at present is the missing member of this series of dimeric complexes. We have not succeeded in isolating such a species, but some unusual new complexes containing molybdenum(IV) have been characterized in the process.

EXPERIMENTAL

All preparations were carried out under rigorously anaerobic (N_2 and Ar gases) conditions using standard procedures involving nylon syringes, stainless-steel needles and Teflon tubing, and rubber seals. The $Mo^{III,III}$ complexes $K[Mo_2(O_2CMe)(OH)_2(edta)]$ and $K_2[Mo_2(OH)_2(NCS)_2(edta)]$,[2] the $Mo^{V,V}$ complex $Na_2[Mo_2O_4(edta)]$,[4] and the $Mo^{VI,VI}$ complex $Na_4[Mo_2O_6(edta)]$ [4] were prepared as previously described. The number of water molecules *n* in samples of $Na_2[Mo_2O_4(edta)]\cdot nH_2O$ varied from 0 to 4 depending on the precise conditions for crystallization. The water is readily removed by storage over P_2O_5 *in vacuo*. The cobalt(III) complexes were as described elsewhere,[6] where in this work chloride salts were used. Other reagents were of AnalaR grade whenever possible, and were used without further purification unless stated.

Preparation of the Sodium Salt of Di-μ-oxo-bis[μ-ethylenediaminetetra-acetato(4—)NN′OO′O″O‴*-μ-hydroxo-μ-oxo-molybdate*(III,IV)]. The $Mo^{III,III}$ dimer, $K[Mo_2(O_2CMe)(OH)_2(edta)]$ (1.0 g, 1.63 × 10^{-3} mol) and sodium azide (0.105 g, 1.63 × 10^{-3} mol; B.D.H., G.P.R., was recrystallized by the addition of ethanol to a saturated solution) were mixed and water (70 ml) was added (reactants both 0.023M). The solution was left for *ca.* 10 h at room temperature by which time it was a wine-red colour. Sodium acetate trihydrate (10 g, Fisons A.R.) was added to induce crystallization. The latter gives a weakly alkaline solution. The product is stable at pH 6—10 and possibly higher. Crystallization took place over a few days at 0 °C, to give intensely red (appearance black) crystals. These were filtered off and washed with ethanol; yield *ca.* 0.35 g (32%) {Found: C, 18.1; H, 3.4; Mo, 28.0; N, 4.2; Na, 6.71%. Calc. for $Na_4[Mo_4O_4(OH)_2(edta)_2]\cdot 12H_2O$: C, 17.6; H, 3.7; Mo, 28.1; N, 4.1; Na, 6.73%}. The number of oxidizing equivalents consumed per Mo was determined by addition of Fe^{III} and back titration with Ce^{IV}, as well as addition of $[VO_2]^+$ and titration of excess of $[VO_2]^+$ with Fe^{II}, and found to be 2.48, indicating an oxidation state of 3.5. The molecules of water of crystallization were as given by the best fit to analytical data.

Preparation of Potassium Salt of Di-μ-oxo-bis[μ-ethylenediaminetetra-acetato(4—)NN′OO′O″O‴*-μ-hydroxo-μ-oxodimolybdate*(III,IV)].—The procedure was essentially the same as for the sodium salt. The $Mo^{III,III}$ dimer $K[Mo_2(O_2CMe)(OH)_2(edta)]$ (0.28 g, 4.5 × 10^{-4} mol) and potassium azide (0.037 g, 4.5 × 10^{-4} mol; Kodak Ltd.) were dissolved in water (10 ml). After a few hours potassium acetate (1.3 g; B.D.H., G.P.R., recrystallized by addition of ether to an ethanolic solution) was added. Crystallisation required 2 weeks at 0 °C. The crystals were filtered off and washed with ethanol; yield *ca.* 80 mg {Found: C, 16.2; H, 3.80; K, 10.4; Mo, 26.0; N, 3.95. Calc. for $K_4[Mo_4O_4(OH)_2(edta)_2]\cdot 16H_2O$: C, 16.0; H, 3.89; K, 10.4; Mo, 25.5; N, 3.73%}. By titration the number of oxidizing equivalents per Mo was found to be 2.45.

Preparation of Sodium Salt of Di-μ-oxo-bis[μ-ethylenedi-

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[1] G. G. Kneale, A. J. Geddes, Y. Sasaki, T. Shibahara, and A. G. Sykes, *J.C.S. Chem. Comm.*, 1975, 356.

[2] G. G. Kneale and A. J. Geddes, *Acta Cryst.*, 1975, **B31**, 1233.

[3] T. Shibahara and A. G. Sykes, preceding paper.

[4] Y. Sasaki and A. G. Sykes, *J.C.S. Dalton*, 1974, 1468.

[5] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301; M. Naarová, J. Padlahová, and J. Podlahá, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1991.

[6] See *e.g.* G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 638.

aminetetra-acetato(4−)NN′OO′O″O‴-*di-μ-oxo-dimolybdate*-(IV,IV)].—A solution of the Mo^{III,IV} tetramer $Na_4[Mo_4O_4(OH)_2(edta)_2]\cdot12H_2O$ (0.6 g) in H_2O (13 ml) was prepared (3.5×10^{-2}M) and filtered. A stream of oxygen gas was bubbled through the solution for *ca.* 3 min, during which time the colour changed from wine-red to a maroon–purple colour. Sodium chloride (2 g, B.D.H., A.R.) was added, and nitrogen gas then passed through the solution to prevent further oxidation. After several hours at 0 °C dark crystals were filtered off and washed with ethanol; yield 0.55 g (94%). If Mo^{III,IV} peaks are still present in the solution spectrum (see below for details), the above reaction with O_2 was repeated {Found: C, 17.8; H, 3.8; Mo, 29.0; N, 4.1; Na, 6.95%. Calc. for $Na_4[Mo_4O_6(edta)_2]\cdot10H_2O$: C, 18.1; H, 3.34; Mo, 28.9; N, 4.22; Na, 6.92%}. Partially oxidized samples of this Mo^{IV,IV} tetramer can be recrystallized by dissolution in water and addition of sodium chloride. Crystals for the *X*-ray crystal study were filtered off under a N_2 stream and were not washed with ethanol. The number of oxidizing equivalents required per Mo was found to be 1.98, indicating a Mo oxidation state of IV.

Preparation of the Polymeric Mo^{IV}*–edta Complex.*—Preliminary spectrophotometric studies on the reaction of the Mo^{III,III} dimer, $K[Mo_2(O_2CMe)(OH)_2(edta)]$ (2×10^{-3}M), with $Na_4[Mo_2O_6(edta)]$ (disappearance of Mo^{III,III} peak at 750 nm, appearance of new peak at *ca.* 550 nm), indicated a stoicheiometry 2 Mo^{III} : 1 Mo^{IV}. Even with Mo^{IV} in large excess (reaction times *ca.* 30 min) no further reaction was observed. To isolate the product the following procedure was adopted. The Mo^{III,III} dimer (0.3 g) and Mo^{VI,VI} dimer (0.2 g) were dissolved in water (20 ml). The solution became dark brown after 2 h. Further treatment was in air. Saturated $BaCl_2$ (B.D.H., A.R.) was added, and a dark red solid was filtered off. To increase the solubility Ba^{2+} ions were exchanged for Na^+ (stirring time, 1 h) using a Dowex 50W-X12 ion-exchange resin charged with Na^+. After separating off the resin methanol was slowly added. The dark red solid was filtered off and washed with methanol and ether. The solid is very resistant to aerial oxidation (unlike the Mo^{IV,IV} tetramer) and could be recrystallised from hot water in air.

The same complex was obtained by heating on a steam-bath for *ca.* 10 h equimolar amounts (1.4×10^{-2}M) of $K[Mo_2(O_2CMe)(OH)_2(edta)]$ (1.06 g) and $Na_2[Mo_2O_4(edta)]$ (1.08 g) in water (120 ml). Supplementary amounts of water were added at intervals. Finally the volume was reduced on a rotary evaporator. The solid was filtered off, washed with a little water, and then ethanol and ether; yield 0.36 g. Recrystallization was from water (20 ml). A Dowex 50W–X12 ion-exchange resin in the Na^+ form was used to exchange K^+ for Na^+. Solid was obtained by addition of methanol and storage of the solution at 0 °C for several hours. The solid was filtered off and washed with methanol; yield 0.27 g (Found: C, 19.6; H, 3.9; Mo, 32.1; N, 4.3; Na, 4.75). The Mo : C ratio is consistent with 2 Mo to each edta. Titration of the Mo indicates that all the Mo is in oxidation state IV. On passing an aqueous solution of complex down a Dowex 50W–X8 cation-exchange resin column the complex was strongly held by the column. Thus the band was not eluted with 4M-$NaClO_4$ whereas in separate experiments $[Mo_2O_4(edta)]^{2-}$ was eluted with 1M-$NaClO_4$ and $[Mo(CN)_8]^{4-}$ moved slowly with 2M-$NaClO_4$. It is concluded that the complex is polymeric with high negative charge.

Molybdate(VI), MoO_4^{2-}, also reacts with the Mo^{III,III} dimer to give a red solution. This reaction and the product were not investigated further.

Determination of N_2 *and* NH_3.—Nitrogen, evolved when equimolar (4.7×10^{-4} mol) amounts of Mo^{III,III} dimer $K[Mo_2(O_2CMe)(OH)_2(edta)]$ and KN_3 were allowed to react in water, was collected by displacement of water in an inverted burette (thermostatted 20 °C). After 20 h evolution of gas ceased. The volume 10.45 ml was corrected for water-vapour pressure. The molar ratio $N_2 : N_3^-$ was 0.98. The amount of ammonia present was determined by adding an excess of concentrated NaOH solution and distilling off the liberated ammonia into a saturated solution of boric acid.[7] A molar ratio $NH_3 : N_3^-$ of 0.96 was obtained.

Magnetic Measurements.—Magnetic susceptibilities were determined on powdered samples at room temperature using a Gouy-balance calibrated with mercury(II) tetrathiocyanatocobaltate(II). The susceptibilities (per tetramer) were for the Mo^{III,IV} complex -499×10^{-6} c.g.s. (Na salt), -428×10^{-6} c.g.s. (K salt) and for the Mo^{IV,IV} complex (Na salt) -50×10^{-6} c.g.s.* The polymeric Mo^{IV} complex is also diamagnetic as shown by magnetic measurements at room temperature.

Reduction Potential.—This was determined for the tetrameric Mo^{IV,IV} and Mo^{III,IV} complexes (Na salts) by a procedure essentially as previously described.[8] The electrode solution consisted of 1.1×10^{-3}M tetramer concentrations in collidine (2,4,6-trimethylpyridine)buffer pH 7.43, $I = 0.12$M (NaCl). A bright platinum electrode was used. Measurements were against a calomel electrode (0.244 V). Salt-bridge solutions of 4M-NaCl and 4M-NH_4NO_3 were exchanged without effect and solutions were thermostatted at 25 °C. As a check on the procedure adopted the Fe^{III}/Fe^{II} reduction potential was measured and found to be 0.742 V with respect to H_2, in good agreement with a value 0.741 V in 1M-$HClO_4$ obtained by Schumb *et al.*[9] The solution of tetramers was diluted ten-fold with buffer, $I = 0.10$M, when the same potential was obtained. An attempt was also made to determine the reduction potential of the Mo^{V,V} dimer $[Mo_2O_4(edta)]^{2-}$ and Mo^{IV,IV} tetramer couple. No constant potential was observed over a 4 h period.

RESULTS

Formation and Properties of the Mo^{III,IV} *Tetramer.*—The spectrum of the Mo^{III,IV} tetramer is shown in Figure 1. Details of peak positions λ (nm), ε (l mol^{-1} cm^{-1}; per tetramer) are: 325 (6 400), 380 (4 640), 473 (7 600), 536 (7 040), and 730 (3 300). To investigate the nature of the reaction of Mo^{III,III} dimer with azide in water (no buffering) a series of solutions was prepared (Table). Final spectra were taken after one day and the % Mo^{III,IV} tetramer obtained from the 473 nm absorption. The highest yield of tetramer was obtained for a 1 : 1 ratio. No evidence for the Mo^{IV,IV} tetramer (detailed examination of spectra) was obtained providing strictly anaerobic conditions were maintained. At still higher azide ratios (25 : 1) the red

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* To convert molar susceptibilty from c.g.s, to SI multiply by $4\pi \times 10^{-6}$.

[7] A. I. Vogel, 'Quantitative Inorganic Analysis,' 3rd edn., Longmans, 1961, p. 257.

[8] W. C. E. Higginson and A. G. Sykes, *J. Chem. Soc.*, 1962, 2841.

[9] W. C. Schumb, M. S. Scherrill, and S. B. Sweatser, *J. Amer. Chem. Soc.*, 1937, **59**, 2360.

colour of the $Mo^{III,IV}$ tetramer was still observed. For such experiments the characteristic peak of the $Mo^{V,V}$ dimer, $[Mo_2O_4(edta)]^{2-}$, at 297 nm (ε 8 980 l mol^{-1} cm^{-1}, per dimer) [4] was distinct. When azide was used in excess it was always detected (deeper red colour with $FeCl_3$) after several days, thus ruling out azide decomposition. No change in spectrum was observed over 24 h on mixing $Mo^{III,IV}$ tetramer (3.5×10^{-5}M) and azide (4.2×10^{-4}M) in water at 25 °C.

The effect of pH and acetate on the reaction of $Mo^{III,III}$ dimer and azide were investigated. A solution of $Mo^{III,III}$ dimer (10^{-2}M) gave a pH of 4.2, and when an equimolar amount of azide was added (final concentrations 0.8×10^{-2}M) the pH was 6.0. This solution reacted (overnight period) to give the wine-red colour of the $Mo^{III,IV}$ tetramer. If the pH was adjusted to 8.0 using sodium acetate–NaOH or triethanolamine–HCl buffer the reaction was more rapid and complete within 2 h. No reaction was observed if the pH was maintained at 4.7 using 0.1M-sodium acetate–acetic acid buffer. A very slow reaction (1 day) was observed if HCl is used instead of acetate buffer to adjust the pH to *ca.* 4.0.

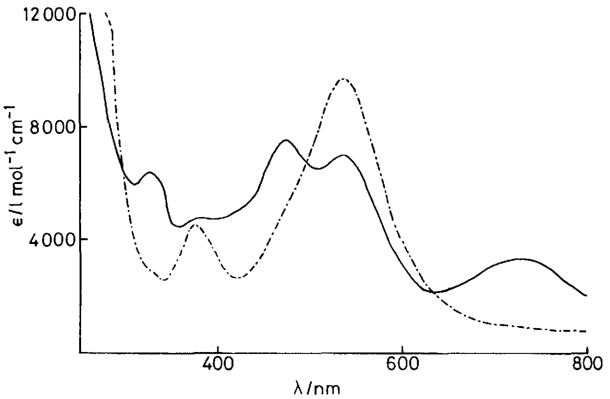

FIGURE 1 U.v.–visible spectrum of the $Mo^{III,IV}$ tetramer (solid line) and $Mo^{IV,IV}$ tetramer (broken line) in water. Absorption coefficients (ε) are per tetramer

TABLE

Reaction of the $Mo^{III,III}$ dimer, $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, with azide in water, and yield of $Mo^{III,IV}$ tetramer as determined from the absorption at 473 nm

$10^3[Mo^{III,III}]$ M	$10^3[KN_3]$ M	Ratio of reactants	$Mo^{III,IV}$ tetramer [a] (%)
9.52	2.38	0.25	13
9.10	4.55	0.50	27
8.77	6.15	0 70	36
8.34	8.34	1.0	37
7.64	11.5	1.5	27
7.14	14.3	2.0	25
5.55	28.6	4.0	23
3.85	57.1	8.0	20

[a] Solutions diluted to permit spectrophotometric determination.

For a reaction with azide in 50-fold excess at pH 8 (0.1M triethanolamine–HCl buffer) spectra gave varying cross-over points (no isosbestic), and the absorbance at 750 nm decreased at first and then increased. This suggested that there are at least two slow stages in the reaction.

Attempts were made to use the $Mo^{III,III}$ dimer with two thiocyanate ligands instead of the μ-acetate. No reaction with azide was observed at pH 8 in 0.1M-triethanolamine–HCl buffer. The reaction of the μ-acetato-$Mo^{III,III}$ dimer with hydrazine instead of azide was observed to give a red colour indicative of the $Mo^{III,IV}$ tetramer (spectrum).

The $Mo^{III,IV}$ tetramer is stable for several hours in 0.1M-H_3BO_3–NaOH buffer in the pH range, 6—10, investigated. The spectrum changes slowly in acid solutions (sodium acetate–acetic acid or KH_2PO_4–NaOH buffer); for example, at pH 3.6 there is a 5% decrease in absorbance at 473 nm within 30 min.

Addition of $[Co(NH_3)_5Cl]^{2+}$ gave a rapid (stopped-flow) oxidation of $Mo^{III,IV}$ tetramer. Before oxidation to the $Mo^{IV,IV}$ tetramer is complete further oxidation of this complex to the $Mo^{V,V}$ dimer $[Mo_2O_4(edta)]^{2-}$ occurred. The reduction potential for the couple involving the two tetramers, (1), was found to be +0.07 V at 25 °C, I = 0.12M (NaCl).

$$[Mo^{IV,IV}{}_2]^{4-} + 2e^- + 2H^+ \longrightarrow [Mo^{III,IV}{}_2]^{4-} \quad (1)$$

Formation and Properties of the $Mo^{IV,IV}$ *Tetramer.*—The preparative procedure described requires relatively concentrated $Mo^{III,IV}$ tetramer (3.5×10^{-2}M) and controlled O_2 access. When oxygen is bubbled through a 10^{-5}M-solution (without buffer) the colour change to the yellow $Mo^{V,V}$ dimer, $[Mo_2O_4(edta)]^{2-}$, is rapid, and no intermediate formation of the $Mo^{IV,IV}$ tetramer was detected. Reaction of the $Mo^{IV,IV}$ tetramer with O_2 to give $[Mo_2O_4(edta)]^{2-}$ was also shown to be rapid and quantitative, but isosbestic points are not retained indicating some intermediate species.

The spectrum of the $Mo^{IV,IV}$ tetramer is shown in Figure 1. Peak positions λ (nm), ε (l mol^{-1} cm^{-1}, per tetramer) are 377 (4 540) and 536 (9 700). The complex is stable in air-free conditions for several hours at pH values in the range 7—10 investigated (H_3BO_3–NaOH or collidine–HCl buffer). In acidic solutions (acetic acid–NaOH or KH_2PO_4–NaOH buffer) the complex is less stable, and at pH 3.6 the 536 nm peak decreased by *ca.* 15% in 30 min at 25 °C, and the peak position shifts to 510 nm. On dissolving the complex in 0.1M-$HClO_4$ or 0.1M-*p*-toluenesulphonic acid (7.9×10^{-3}M solution) some dark maroon solid was obtained in 2 h. The supernatant solution became almost colourless within 7 h. The solid was filtered off and washed with ethanol and diethyl ether (yield, 0.10 g). Analyses were Mo (34.6%) and Na (0.18%) the latter indicating a zero-charged complex. The sample gave a strong i.r. band at 960 cm^{-1} corresponding to ν(Mo=O).[10] A firm structural assignment was not possible from our studies. The complex is insoluble in non-aqueous solvents *e.g.* dimethyl sulphoxide, acetonitrile, and tetrahydrofuran.

No reaction of the $Mo^{IV,IV}$ tetramer (8×10^{-5}M) with azide (25-fold excess), or with the $Mo^{V,V}$ dimer (10^{-4}M), was observed at pH 8 within 2 h. Reaction with the $Mo^{III,III}$ dimer (10^{-4}M) occurs at pH 8 (triethanolamine–HCl buffer), and formation of an equimolar amount of $Mo^{III,IV}$ tetramer is observed within 15 min with retention of an isosbestic. From final spectra it can be concluded that an equation yielding a greater than equimolar portion of $Mo^{III,IV}$ tetramer (2) does not apply. An alternative (3)

$$2Mo^{III,III} + Mo^{IV,IV}{}_2 \longrightarrow 2Mo^{III,IV}{}_2 \quad (2)$$

in which the Mo^{IV} polymer is generated is possible since

$$Mo^{III,III} + Mo^{IV,IV}{}_2 \longrightarrow Mo^{III,IV}{}_2 + Mo^{IV}{}_n \quad (3)$$

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[10] See *e.g.* M. Novotny and S. J. Lippard, *Inorg. Chem.*, 1974, **13**, 828.

polymeric Mo^{IV} is known to have a weak absorbance (see below).

The $Mo^{IV,IV}$ tetramer (10^{-4}M) is rapidly oxidized by $[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$ (all in 50-fold excess), $t_{\frac{1}{2}} \leqslant 1$ min. By microsyringe addition of the oxidant it was demonstrated that in the first two instances at least isosbestics were not retained.

Formation and Properties of Polymeric Mo^{IV}*-edta*.—The spectrum (Figure 2) is notable for the much smaller ε values as compared to those in Figure 1. A peak is observed at 550 nm (ε 136 l mol^{-1} cm^{-1}) and a shoulder at 310 nm (ε 500 l mol^{-1} cm^{-1}), where absorption coefficients are per Mo atom. When dissolved in 1M-*p*-toluenesulphonic acid the absorption spectrum decreased over 1 day. The final spectrum after 3 days gave a peak at 505 nm (ε 61 l mol^{-1} cm^{-1} per Mo) which strongly suggests the formation of the Mo^{IV} aqua-ion.[11] In view of the uncertainty regarding the precise composition of the polymer other reactions were not investigated.

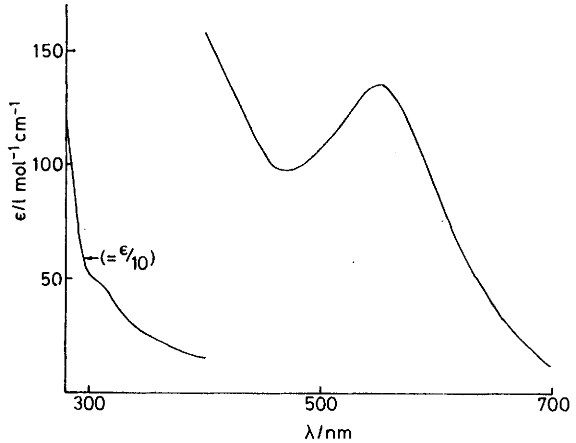
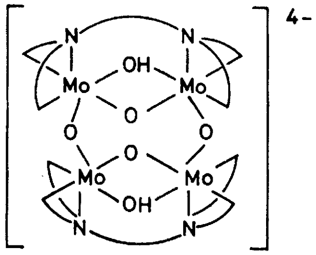


FIGURE 2 U.v.–visible spectrum of the Mo^{IV} polymer in water. Absorption coefficients (ε) are per Mo

DISCUSSION

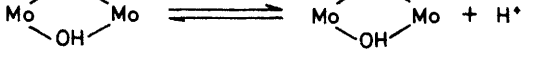
An *X*-ray crystal structure of the $Mo^{III,IV}$–edta complex (K^+ salt) obtained by azide oxidation of the $Mo^{III,III}$ dimer has shown this to be a tetrameric species,[12] $K_4[Mo_4O_4(OH)_2(edta)_2]$, with 16 water molecules of crystallisation. The complex is diamagnetic,



and all bridging groups are symmetrically disposed (equal bond lengths) to adjacent Mo atoms. The molybdenum atoms are, therefore, to be regarded as identical with a mixed oxidation state of 3.5. A short Mo–Mo distance of 2.41 Å (consistent with metal–metal bonding) is observed at the μ-oxo-μ-hydroxo-bridged sites. The Mo–OH bond lengths are clearly longer than those Mo–O (bridging).

The $Mo^{IV,IV}$ product obtained by controlled oxidation, with O_2, of the $Mo^{III,IV}$ tetramer, is also tetrameric from preliminary *X*-ray studies.[13] The structure appears to be basically the same as that of the $Mo^{III,IV}$ tetramer except that all the bridges are μ-oxo.

The reaction of the $Mo^{III,III}$ dimer with azide has been studied with and without addition of acetate and at various pH values from 4—8. No reaction is observed at pH 4.7 (pK_a for HN_3 is 4.68 at 20 °C)[14] in the presence of free acetate, but reaction does occur slowly when no acetate is present. Displacement of the acetate would seem to favour reaction. As the pH is increased to 8 (even in the presence of acetate) the rate increases markedly. This increased reactivity corresponds to acid dissociation at one of the hydroxo-bridges [reaction



(4)

(4)] pK_a 7.73 at 0 °C,[3] when the $Mo^{III,III}$ reactant assumes a bridging structure similar to that of the $Mo^{III,IV}$ product. Furthermore, no reaction of the $Mo^{III,III}$ complex with two thiocyanate ligands replacing the μ-acetato-group is observed with azide at pH 8. Since the latter complex also undergoes acid dissociation at a μ-hydroxo-bridge,[3] it is concluded that co-ordination of azide must precede reaction.

The products of the $Mo^{III,III}$ reaction with azide are the $Mo^{III,IV}$ tetramer and $Mo^{V,V}$ dimer. Quantitative formation of N_2 and NH_3 is observed, consistent with equations (5) and (6). Maximum yield (37%) of the

$$2Mo^{III,III} + N_3^- \xrightarrow{H^+} Mo^{III,IV}{}_2 + N_2 + NH_3 \quad (5)$$

$$Mo^{III,III} + 2N_3^- \xrightarrow{H^+} Mo^{V,V} + 2N_2 + 2NH_3 \quad (6)$$

$Mo^{III,IV}$ tetramer was observed for a 1 : 1 ratio of reactants. Competition between $Mo^{III,III}$ and N_3^- for further reaction with an intermediate is implied. Since co-ordinated azide is in a strong position to bring about a two-equivalent change we tentatively suggest that this intermediate is a $Mo^{IV,IV}$ dimer. Thus a possible reaction scheme is (7). No $Mo^{IV,IV}$ tetramer formation is observed.

$$\begin{tikzcd} \mathrm{Mo^{III,III}} \arrow[r, "+\mathrm{N_3^-}"] & \mathrm{Mo^{IV,IV}} \arrow[r, "+\mathrm{N_3^-}"] \arrow[d, "+\mathrm{Mo^{III,III}}"] & \mathrm{Mo^{V,V}} \quad (7) \\ & \mathrm{Mo^{III,IV}{}_2} & \end{tikzcd}$$

More than one stage is observed (isosbestics not retained) in each of the $Mo^{III,IV}{}_2 \longrightarrow Mo^{IV,IV}{}_2 \longrightarrow Mo^{V,V}$

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[11] M. Ardon and A. Pernick, *J. Amer. Chem. Soc.*, 1973, **95**, 6871; J. F. Ojo, Y. Sasaki, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, 1976, **15**, 1006.

[12] T. Shibahara, B. Sheldrick, and A. G. Sykes, *J.C.S. Chem. Comm.*, 1976, 523.

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conversions. The reduction potential of $+0.07$ V for the couple involving the two tetramers points to the $\mathrm{Mo^{III,IV}}$ tetramer being a strong reducing agent. Although the reduction potential of the $\mathrm{Mo^{IV,IV}{}_2/Mo^{V,V}}$ couple could not be determined, the $\mathrm{Mo^{IV,IV}}$ tetramer also exhibits strong reducing properties. Thus the reactions with mild oxidants such as $[\mathrm{Co(NH_3)_5Cl}]^{2+}$ are rapid ($t_{\frac{1}{2}} < 1$ min) for both tetrameric species. The $\mathrm{Mo^{V,V}}$ product does not retain a tetrameric structure presumably because of the need to provide terminal oxo-groups for $\mathrm{Mo^{V}}$. Only by cleavage of the two single oxo-bridges of the $\mathrm{Mo^{IV,IV}}$ tetramer can this be achieved.

The reactions of both tetramers with O_2 are of interest in that there is no site for the O_2 to co-ordinate unless the co-ordination number is increased. An outer-sphere $O_2 \longrightarrow O_2^-$ change is implied. In the case of the $\mathrm{Mo^{III,IV}}$ tetramer at least, a calculated value of the reduction potential for the O_2/O_2^- couple of -0.38 V [15] seems incompatible with observed behaviour. Taube and colleagues [16] have made this same point with regard to the O_2 oxidation of $[\mathrm{Ru(NH_3)_6}]^{2+}$.

Conditions for the formation of the $\mathrm{Mo^{IV,IV}}$ tetramer are *via* the $\mathrm{Mo^{III,IV}}$ analogue. When the $\mathrm{Mo^{III,III}}$ complex is oxidized with O_2, rapid conversion to the $\mathrm{Mo^{V,V}}$ dimer is observed with no intermediate red colour. When the $\mathrm{Mo^{III,III}}$ complex is oxidized by $\mathrm{Mo^{VI,VI}}$ and (more reluctantly) $\mathrm{Mo^{V,V}}$, the product is polymeric $\mathrm{Mo^{IV}}$. Only with N_2H_4 as oxidant have we as yet been able to observe formation of the tetrameric $\mathrm{Mo^{III,IV}}$ species as in the oxidation with N_3^-.

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