Preparation and Characterization of Dimeric Molybdenum(III)–Ethylenediaminetetra-acetate Complexes

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The potassium salt of the complex μ-acetato-μ-ethylenediaminetetra-acetato(4—)*NN′OO′O″O‴*-di-μ-hydroxo-dimolybdate(III), $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, (1), has been prepared by the Zn–Hg reduction of the molybdenum(V) dimer $[Mo_2O_4(edta)]^{2-}$, in acetate buffer, pH 5. At pH values in the range 3—4, with and without acetate, a water-insoluble molybdenum(III) product, (2), is obtained whose analysis is consistent with its formulation as $[Mo_2(OH)_2(H_2O)_2(edta)]$. The bisthiocyanato-complex $[Mo_2(OH)_2(NCS)_2(edta)]^{2-}$ (3) has been isolated following treatment of (1) with thiocyanate. All three complexes are diamagnetic which is consistent with the presence of metal–metal bonding. From a comparison of solution and diffuse reflectance u.v.–visible spectra, it is concluded that complexes (2) and (3), like complex (1), have a di-μ-hydroxo-structure. Complexes (1) and (3) give reversible spectrophotometric changes in the pH range 4—12, and pH titrations indicate one end-point corresponding to the formation of μ-oxo-μ-hydroxo-species pK_a 7.73 for (1) at 0 °C and 7.29 for (3) at *ca.* 20 °C. Effects resulting from the addition of the acids *p*-toluenesulphonic acid, H_3PO_4, and H_2SO_4 to (1) are considered. Analogues of complex (1) with formate replacing acetate, (4), and hedta (*N*-hydroxyethylethylenediaminetriacetate) replacing edta, (5), have also been prepared.

ETHYLENEDIAMINETETRA-ACETATO (edta) complexes of molybdenum-(V) [1] and -(VI) [2] are now well characterized. The molybdenum(V) complex $[Mo_2O_4(edta)]^{2-}$ contains a single edta co-ordinated to both metal atoms of the di-μ-oxo Mo_2O_4 unit. With molybdenum(VI) a 2 : 1 complex $[Mo_2O_6(edta)]^{4-}$ is also formed, but in this case the Mo atoms remain remote from each other and co-

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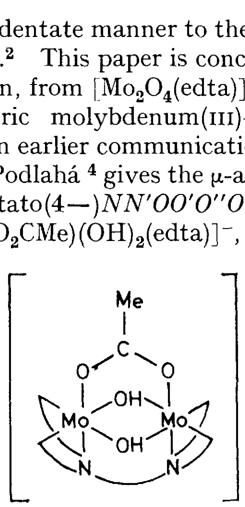
[1] L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, 1967, **6**, 2146.

[2] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301

ordinated in a tridentate manner to the two halves of the edta respectively.[2] This paper is concerned with details of the preparation, from $[Mo_2O_4(edta)]^{2-}$, and characterization of dimeric molybdenum(III)–edta complexes. As indicated in an earlier communication [3] the procedure of Kloubek and Podlahá [4] gives the μ-acetato-μ-ethylenediaminetetra-acetato(4–)*NN′OO′O″O‴*-di-μ-hydroxo-complex, $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, (1). An *X*-ray crystal structure of (1) has been carried out.[5] The isolation of (1) and related complexes, together with properties relating to their characterisation are reported in this paper.



(1)

EXPERIMENTAL

Reagents were of AnalaR Grade purity, and were in most cases used without further purification. *p*-Toluenesulphonic acid (Aldrich Chem. Co.), hereafter Hpts, was recrystallised from water. Molybdenum(III) is air sensitive and all procedures were carried out under an atmosphere of nitrogen using Teflon tubing, syringe, and rubber serum cap techniques in order to deoxygenate and transfer solutions.

Preparation of Potassium μ-*Acetato*-μ-*ethylenediaminetetra-acetato*(4–)NN′OO′O″O‴-*di*-μ-*hydroxo-dimolybdate*(III) *Dihydrate* $K[Mo_2(O_2CMe)(OH)_2(edta)]\cdot 2H_2O$, *Complex* (1).—Potassium acetate (12 g) was dissolved in water (50 ml) and the pH adjusted to 5.0 by addition of glacial acetic acid (*ca.* 5 ml). The complex $Na_2[Mo_2O_4(edta)]$ (2.0 g), prepared as described previously,[6] was dissolved in the above to give a 6.2×10^{-2}M-solution of complex in *ca.* 3M-acetate buffer. The solution was reduced by shaking vigorously for *ca.* 30 min with amalgamated zinc (10 g), which was prepared by treating 8—30 mesh zinc shot with mercury(II) chloride. A green precipitate formed within a few minutes. The solution was cooled at 0 °C for 3—4 h, and the green precipitate separated from the amalgamated zinc by decantation and then filtration. The solid was washed with cold water, ethanol, and finally diethyl ether, yield 1.5 g (72%) {Found: Mo, 29.1; C, 21.5; H, 3.7; N, 4.3; H_2O, 6.05%. Calc. for $K[Mo_2(O_2CMe)(OH)_2(C_{10}H_{12}N_2O_8)]\cdot 2H_2O$: Mo, 29.6; C, 22.2; H, 3.27; N, 4.32; H_2O, 5.56%}.

Preparation of Potassium μ-*Acetato*-μ-*ethylenediaminetetra-acetato*(4–)NN′OO′O″O‴-*di*-μ-*hydroxo-dimolybdate*(III), $K[Mo_2(O_2CMe)(OH)_2(edta)]$, *Anhydrous Form of* (1).—Essentially the same electrolytic procedure as that of Kloubek and Podlahá was used.[4] A solution of $Na_2[Mo_2O_4(edta)]$ in 0.2M-acetate buffer (pH 3—4) was used in the cathode compartment. The electrolysis required 8—10 h after which KCl was added to the resultant green solution. Green crystals were filtered off and washed with ethanol and diethyl ether; yields <20%. The anhydrous form of the complex was also obtained by dissolving 1 g of the dihydrate (obtained by reduction with zinc amalgam) in 50 ml of water, and adding KCl (*ca.* 7 g). After cooling at 0 °C green crystals were filtered off and washed with ethanol and diethyl ether; yield 0.8 g (83%) {Found: Mo, 31.3; C, 23.4; H, 2.8; N, 4.5. Calc. for $K[Mo_2(O_2CMe)(OH)_2(C_{10}H_{12}N_2O_8)]$: Mo, 31.34; C, 23.5; H, 2.80; N, 4.58%}.

Preparation of μ-*Ethylenediaminetetra-acetato*(4–)NN′OO′O″O‴-*di*-μ-*hydroxo-bis*[*aquamolybdenum*(III)], *Complex* (2).—A solution of $Na_2[Mo_2O_4(edta)]$ (1.1 g) in 1M-acetate buffer (20 ml) at pH 3 was reduced electrolytically as previously described.[4] A blue-green solid, which formed during the electrolysis (4 h), was filtered off and washed with water, ethanol, and diethyl ether; yield 0.15 g (8%). The same complex was obtained on electrolysis of $Na_2[Mo_2O_4(edta)]$ (1.18 g) in 40 ml of hydrochloric acid the pH of which (monitored on a Radiometer GK2322C combined electrode) was maintained in the range 3—4 by addition of 1M-HCl as required; yield after 5 h, 0.26 g (24%) {Found: C, 21.85; H, 3.5; N, 5.25%. Calc. for $[Mo_2(OH)_2(H_2O)_2(C_{10}H_{12}N_2O_8)]$: C, 21.83; H, 3.29; N, 5.09%}.

Preparation of μ-*Ethylenediaminetetra-acetato*(4–)NN′OO′O″O‴-*di*-μ-*hydroxo-bis*[*thiocyanatomolybdenum*(III)], *Complex* (3).—An excess of potassium thiocyanate (5.0 g) and the anhydrous form of complex (1) (1.0 g) were added to 30 ml of water and the suspension was shaken vigorously for 3 h. The initial complex reacted and dissolved within this period. The product was obtained when the mixture was set aside at 0 °C. The dark green crystals were filtered off and washed several times with ethanol and diethyl ether; yield 1.12 g (90%) {Found: C, 18.9; H, 3.30; K, 10.1; Mo, 25.0; N, 7.6; S, 8.5; H_2O, 8.4%. Calc. for $K_2[Mo_2(OH)_2(NCS)_2(C_{10}H_{12}N_2O_8)]$: C, 18.8; H, 2.64; K, 10.24; Mo, 25.15; N, 7.34; S, 8.41; H_2O, 7.1%}.

Preparation of Potassium μ-*Ethylenediaminetetra-acetato*-(4–)NN′OO′O″O‴-μ-*formato-di*-μ-*hydroxo-dimolybdate*(III) *Dihydrate*, $K[Mo_2(O_2CH)(OH)_2(edta)]\cdot 2H_2O$, *Complex* (4).—Solid KOH (13 g) was added to formic acid (10 ml, Fisons A.R.) in water (50 ml) to adjust the pH to *ca.* 4.5. The solution (*ca.* 4.4M in formate) was added to $Na_2[Mo_2O_4(edta)]$ (2.0 g) which was then transferred to a vessel containing amalgamated zinc (10 g). This was shaken to give a green solution after 10 min. The solution was filtered and ethanol (40 ml) was added to it when a gelatinous precipitate was obtained. This was filtered off, washed with 40 ml ethanol (× 5) to remove potassium formate, and then ether; yield 1.4 g (70%) {Found: C, 19.4; H, 3.0; N, 4.2; H_2O, 6.3%. Calc. for $K[Mo_2(O_2CH)(OH)_2(C_{10}H_{12}O_8N_2)]\cdot 2H_2O$: C, 20.8; H, 3.02; N, 4.42; H_2O, 5.7%}.

Preparation of μ-*Acetato-di*-μ-*hydroxo*-μ-*hydroxyethylethylenediaminetriacetato*(4–)NN′OO′O″O‴-*dimolybdenum*(III), *Complex* (5).—The Mo^V complex $K[Mo_2O_4(hedta)]\cdot 2H_2O$ (one H_2O is probably co-ordinated) was first prepared, where hedta is the hydroxyethylethylenediaminetriacetato-ligand {Found: C, 19.2; H, 2.7; N, 4.45%. Calc. for $K[Mo_2O_4(C_{10}H_{15}N_2O_7)]\cdot 2H_2O$: C, 19.2; H, 3.39; N, 4.49%}. The same procedure as described for complex (1) was used. After the reaction mixture had been shaken with amalgamated zinc for *ca.* 1 h a green precipitate was

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

[4] J. Kloubek and J. Podlahá, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2981.

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

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

obtained which was decanted off and washed with ethanol. Samples of the complex gave C/N analyses corresponding to one acetate in addition to the hedta ligand. Solutions in H_2O were not held by either cation- or anion-exchange resin columns suggesting zero charge and a formula $[Mo_2(O_2CMe)(OH)_2(H_2O)(hedta)]$ {Found: C, 21.7; H, 3.65; N, 4.45; Mo, 27.5%. Calc. for $[Mo_2(O_2CCH_3)(OH)_2(C_{10}H_{15}N_2O_7)]\cdot4H_2O$: C, 22.1; H, 4.6; N, 4.31; Mo, 29.5%}. Solid samples contained as much as 3% potassium (a uninegative complex would give K *ca.* 6%).

Conversion of Complex (2) *into Complex* (1).—Complex (2) (0.32 g) was suspended in *ca.* 3M-acetate buffer at pH 5.0 (10 ml). A green solution was obtained after *ca.* 2 h, and complex (1) was obtained from this by addition of KCl.

Reaction of Complex (1) *with* KCN.—A large excess of KCN (3.0 g) in water (5 ml) was added to anhydrous complex (1) (0.28 g). The resulting brown solution was kept at room temperature for 1 day. Ethanol (2 ml) was added slowly when dark green plate-like crystals were obtained. These were filtered off and washed several times with methanol; yield 0.31 g (70%) {Found: C, 18.2; H, 1.2; K, 32.7; Mo, 20.3; N, 21.2; H_2O, 7.75%. Calc. for $K_4[Mo(CN)_7]\cdot2H_2O$: C, 17.9; H, 0.9; K, 33.2; Mo, 20.4; N, 20.8; H_2O, 7.66%}.

Analytical Procedures.—Total molybdenum content was obtained by an established procedure.[7] The oxidation state of molybdenum was determined by the addition of iron(III) and back titration with cerium(IV).[8] Potassium was determined by flame photometry after the solution had been passed through a column of ion-exchange resin (Dowex 1X8–400, chloride form). The C, H, and N values were determined by standard microanalytical techniques, and S as $BaSO_4$ following combustion of the sample. The water of crystallization was determined by weight loss over P_2O_5 *in vacuo*.

Physical Measurements.—U.v.–visible solution and reflectance spectra were recorded on a Unicam SP 500 spectrophotometer. For the diffuse reflectance spectra K_2SO_4 was used as a reference. A plot of log $\{(1-\rho_\infty)^2/2\rho_\infty\}$ against wavelength, where ρ_∞ is the measured transmittance, gives the absorption spectrum of the solid.[9] Magnetic susceptibilities were determined on a powdered sample at room temperature using a Gouy-balance calibrated with mercury(II) tetrathiocyanatocobaltate(II). I.r. spectra were recorded on a Perkin-Elmer 457 instrument over the range 4 000—250 cm^{-1}, using Nujol mull or KBr discs. *X*-Ray powder diagrams were recorded on a Philips *X*-ray set using Cu-K_α radiation. Acid dissociation constants for complexes (1) and (3) were determined by titration with 0.10M-NaOH using a Radiometer pH-meter and GK 2322C combined electrode.

RESULTS AND DISCUSSION

The method for the preparation of complex (1) involving Zn–Hg reduction of the Mo^V dimer $[Mo_2O_4(edta)]^{2-}$ is far more efficient with regard to time and product yield than the electrolytic procedure. The amount of acetate as well as pH is critical in determining whether complex (1) or (2) is obtained. At pH 5 in 3M-acetate the μ-acetato-complex (1) is obtained. At pH 3—4, when acetate is more extensively protonated, and therefore shows less tendency to co-ordinate, the insoluble aqua-complex (2) whose analysis is consistent with its formulation as $[Mo_2(OH)_2(H_2O)_2(edta)]$ is the product. The μ-acetato-complex (1) is also obtained when the initial pH is in the range 3—4 with only *ca.* 0.2M-acetate present. This amount of acetate is insufficient to maintain the pH in view of the high consumption of H^+ for the $Mo^V \longrightarrow Mo^{III}$ conversion. Complex (2) can be converted into (1) by treatment with acetate at pH 5. The thiocyanate complex (3), whose analysis is consistent with its formulation as $[Mo_2(OH)_2(NCS)_2(edta)]^{2-}$ is obtained by treating complex (1) with an excess of thiocyanate. Isosbestics are not retained in this conversion which suggests that replacement occurs in at least two stages. As reported elsewhere[10] the reaction with azide is complicated by redox processes. Thus at pH 8 a red mixed valence (3.5) tetrameric edta complex is obtained in which all four molybdenums are equivalent. The reaction of complex (1) with cyanide yields the well characterized mononuclear $[Mo(CN)_7]^{4-}$ complex in good yield (70%). The spectrum in H_2O is in good agreement with that reported by Gray and his co-workers.[11] Redox titrations of complexes are consistent with both molybdenum atoms being in oxidation state III.

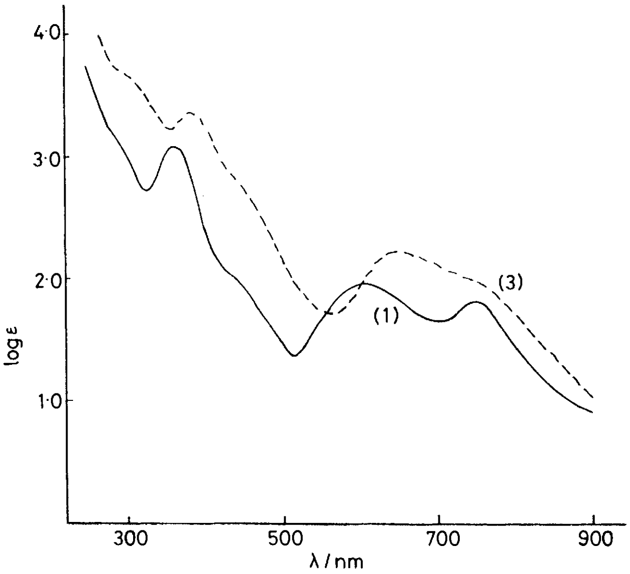

FIGURE 1 Solution spectra in water, pH *ca.* 6, for complexes $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, (1); and $[Mo_2(OH)_2(NCS)_2(edta)]^{2-}$ (3). Absorption coefficients, ε, are in units l mol^{-1} cm^{-1}, *i.e.* per dimer

Features of the *X*-ray structure of complex (1) are that the two Mo octahedra share a common edge containing two bridging O-atoms which are assumed to be protonated to give the anion a uninegative charge. An unusual feature is the presence of two other bridging

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[7] G. G. Rao and M. Swyanarayana, *Z. analyt. Chem.*, 1959, **168**, 177.

[8] A. R. Bowen and H. Taube, *Inorg. Chem.*, 1974, **13**, 2245.

[9] F. Grum, ' Physical Methods of Chemistry,' eds. Weissberger and Rossiter, Wiley, 1972, vol. 1, Part IIIB, p. 292.

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

[11] G. R. Rossman, F. D. Tsay, and H. B. Gray, *Inorg. Chem.*, 1973, **12**, 824.

groups, *viz.* the ethylenediamine of the edta and the acetate. Solution spectra of complexes (1) and (3) (Figure 1) and solid diffuse-reflectance spectra of (1)—(3) (Figure 2) indicate similar structural features in all cases. On this basis structural assignments for (2) and (3) are as illustrated below. Complex (4) is assumed to have the same structure as (1) with formate for acetate. Further details of spectra of (1), (3), and (4) are given in the Table. The hedta complex (5) has a similar spectrum with peaks at 300sh, 361, 430sh, 605, and 755 nm. The complex behaves as a neutral species in solution which suggests that the hydroxyethyl arm is unco-ordinated with an H_2O occupying the available site. The solution spectrum as well as the *X*-ray powder diagram for (1) are similar to those reported by Kloubek and Podlahá.[4] One additional important *X*-ray powder line which we observe in (1) at *ca.* 11.3° * is due to the (022) lattice plane reflection. According to the $F_o - F_c$ table of *X*-ray single-crystal analysis data,[5] the reflection strength due to the (022) lattice plane is one of the strongest reflections, and the *X*-ray powder spectrum of (1) therefore gives a strong reflection at 11.3°.

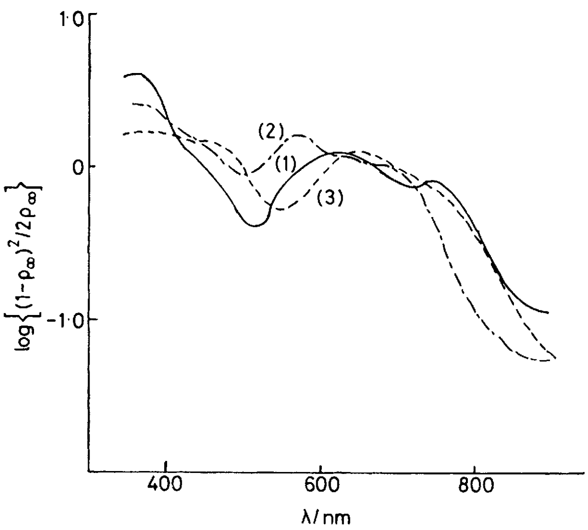
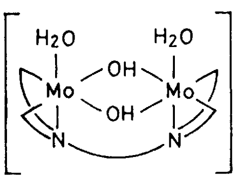
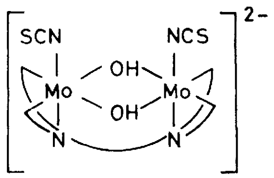


FIGURE 2 Diffuse-reflectance spectra of complexes $[Mo_2(O_2CMe)(OH)_2(edta)]^-$, (1); $[Mo_2(OH)_2(H_2O)_2(edta)]$, (2); and $[Mo_2(OH)_2(NCS)_2(edta)]^{2-}$, (3); where ρ_∞ is the reflectance of an infinitely thick sample



(2)



(3)

The spectrum of (1) is constant over the range pH 4—6 but changes dramatically (green → brown) as the pH is increased to 11.6 (Figure 3). Isosbestic points were observed at 571 and 631 nm. On pH titration it became clear that complex (1) (10^{-2}M) behaves as a monobasic acid, $pK_a = 7.73 \pm 0.03$ at 0 °C, where K_a is the acid dissociation constant (no ionic strength adjustments). Similarly complex (3) gave $pK_a = 7.29 \pm 0.03$ at *ca.* 20 °C. No cross-over points are observed in spectra of (3) at varying pH values. The reactions of both complexes (1) and (3) were shown to be

TABLE

Details of diffuse reflectance and solution spectra, pH *ca.* 6, for complexes (1)—(4)

	$\lambda_{max.}$/nm [a]	λ_{max}/nm [b]	ϵ/l mol^{-1} cm^{-1} [b,c]
$K[Mo_2(O_2CMe)(OH)_2(edta)]\cdot xH_2O$, ($x$ = 0 or 2), (1)			
	750.	750	60
	625	605	81
	435sh	440sh	97
	360	362	1 200
	d	290sh	1 220
$[Mo_2(OH)_2(H_2O)_2(edta)]$, (2)			
	690		
	630sh		
	570		
	430sh		
	365		
$K_2[Mo_2(OH)_2(NCS)_2(edta)]\cdot 3H_2O$, (3)			
	720sh	750sh	91
	650br	650	159
	460	460sh	421
	385	460sh	421
	385	383	2 280
	d	300	4 660
$K_2[Mo_2(O_2CH)(OH)_2(edta)]\cdot 2H_2O$, (4)			
	740	745	46
	600	595	62
	480sh	440sh	75
	375	360	767
	d	290	1 010

[a] Diffuse reflectance, Figure 2. [b] Solution spectra, Figure 1. [c] Solution spectra, ϵ per dimer unit. [d] Not determined.

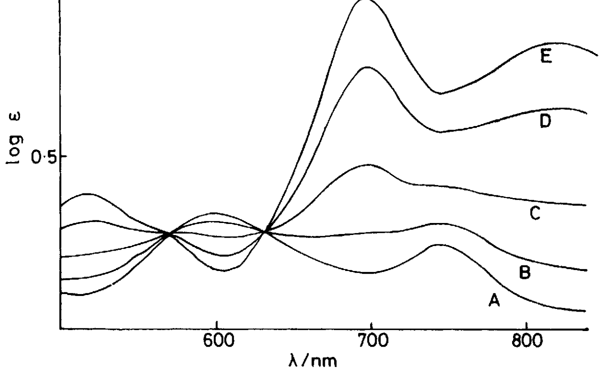


FIGURE 3 Effect of pH on the spectrum of a 4 × 10^{-3}M-solution of $[Mo(O_2CMe)(OH)_2(edta)]^-$, (1), at 0 °C. The pH was varied: 4.2—6.0 (A), 7.37 (B), 7.92 (C), 8.57 (D), and 11.1 (E)

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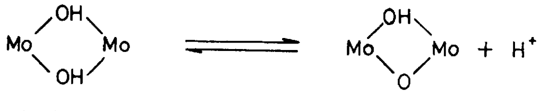
* Peak positions *d* in ref. 4 are given in Å and have been converted into angles (θ) using Bragg's formula $2d\sin\theta = \lambda$.

reversible by addition of HCl. The behaviour observed is accounted for by the reversible acid dissociation (1):



(1)

Solid complex (2) is stable in air for relatively long periods (>1 week), whereas complexes (1) and (3) in the solid and in solution are only stable in air-free conditions. The solid formato-complex (4) decomposes within a few days even under air-free conditions. This decrease in stability (compared to acetate) is attributed to the less basic character of the formate. Solutions of complex (1) (5×10^{-3}M) at pH 4.2 give *ca.* 6% decomposition within 1 h at 25 °C. The green colour is retained for >3 days after which the solution takes on a yellow colour, as $[Mo_2O_4(edta)]^{2-}$, peak at 297 nm,[6] is formed. At pH 8 in 0.3M-tris/HCl buffer a 6.7×10^{-3}M-solution of complex (1) undergoes slow decomposition with the formation of small amounts of the red $Mo^{III,IV}$ tetramer after 3 days.[10] No hydrogen gas was collected and the nature of the reaction, *i.e.* identity of oxidant, is uncertain. Solutions of complex (1) (10^{-2}M), in water or buffered to pH 8, on exposure to air give $[Mo_2O_4(edta)]^{2-}$ and no red colour is observed.

On addition of 0.1M-Hpts (a strong acid the anion of which has poor donor properties) complex (1) gives a precipitate of (2) within 1 h. Complex formation with phosphate and sulphate occurs on addition of 0.1M-H_3PO_4 and 0.1M-H_2SO_4 and no precipitation of (2) is observed. The reactions take *ca.* 10 h at 25 °C to reach completion and give stable (>1 day) species which are a bright green as opposed to a blue-green colour. Cross-over points are observed at 600 and 703 nm for H_3PO_4, and 607 and 716 nm for H_2SO_4. A feature of the reactions are the changes in spectra at 500—800 nm (Figure 4) with loss of one peak. The phosphato-complex gives a peak at 627 nm (ε 98 l mol^{-1} cm^{-1}) and the sulphato-complex at 625 nm (ε 86 l mol^{-1} cm^{-1}). The reaction with 0.1M-H_2SO_4 may be incomplete; higher concentrations of H_2SO_4 resulted in precipitation. Attempts to obtain solid samples of the phosphato- and sulphato-complexes were unsuccessful. Bridging of metal atoms by phosphate and sulphate is known to occur in other systems and is a strong possibility here. Replacement of acetate is likely to precede loss of the edta.

The complexes prepared are diamagnetic with susceptibilities as previously reported.[4] This indicates metal–metal bonding with pairing of the d^3 electrons on each metal. The short Mo–Mo distance of 2.43 Å for complex (1) is consistent with this.[5] A superexchange mechanism operating *via* the hydroxy-bridge could also play some part in generating the diamagnetism. We note that the complexes have peaks in the visible region 600—750 nm with absorption coefficients ε = *ca.* 100 l mol^{-1} cm^{-1}. The Mo^{III} aqua-dimer is reported [12] to have peaks at 572 nm (ε 78 l mol^{-1} cm^{-1}, *i.e.* per dimer unit) and 624 (ε 86 l mol^{-1} cm^{-1}). These peaks seem to be characteristic of Mo^{III} dimers since monomeric $[Mo(H_2O)_6]^{3+}$ and $[MoCl_6]^{3-}$ have no peaks in this region. The bands observed clearly do not originate from *d–d* electronic transitions on a single metal atom. Similarly dimeric Mo^{II} complexes with and without bridging groups are known to give characteristic peaks *ca.* 500 nm.[8]

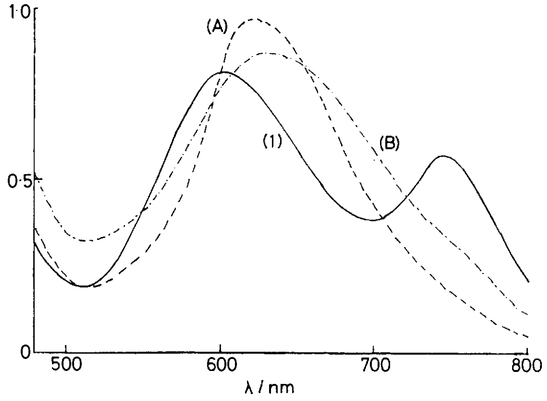


FIGURE 4 The spectrum of 10^{-3}M-$[Mo_2(O_2CMe)(OH)_2(edta)]^-$ (1), and effect of adding H_3PO_4 (A) (1-cm cell) and H_2SO_4 (B) (complex at half concentration, 2-cm cell) to concentrations 0.10M. Reaction time *ca.* 12 h, *ca.* 20 °C

A feature of i.r. spectra of the complexes is the band (cm^{-1}) at 639 for (1), 640 for (2), 628 for (3), and 632 for (4), which is most likely due to the antisymmetric hydroxo-bridge vibrations. Similar vibrations for the di-μ-oxo-Mo^V dimers are at *ca.* 740 cm^{-1}.[13] This is reasonable when the longer bond distance to bridging oxygens, 2.04 Å for Mo^{III} [5] and *ca.* 1.92 Å for Mo^V,[14] is taken into account. The ν(CS) frequency which is generally a good diagnostic method of distinguishing between N- or S-bonded NCS^- could not be identified for complex (3) because of the complexity of the spectrum. Since NCS^- is N-bonded in $[Mo(NCS)_6]^{3-}$,[15] an N-bonded structure seems likely for complex (3).

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[7/384 *Received, 4th March,* 1977]

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