The Behaviour of Trioxo(diethylenetriamine)molybdenum(VI) and Trioxo(diethylenetriamine)tungsten(VI) in Solution

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Kinetic and thermodynamic studies on the reaction of 8-hydroxyquinoline (oxine) with the octahedral complex trioxo(diethylenetriamine)molybdenum(VI), MoO_3(dien), in aqueous solution, give almost identical results to those reported previously for the reaction of oxine with molybdate, MoO_4^{2-}. Raman spectra and conductivity measurements confirm that the complex, MoO_3(dien), is unstable in aqueous solution, and that it is hydrolysed to give molybdate and free diethylenetriamine which is protonated. Although the complex can be precipitated from aqueous solution by the addition of ethanol, in the presence of sodium ions the product is sodium molybdate. The preparation of an analogous tungsten(VI) complex, WO_3(dien), is described, and its solution chemistry shown to be similar to that of MoO_3(dien). Attempts to prepare a chromium(VI) analogue in the solid state or in solution were unsuccessful.

KNOWLES and DIEBLER [1] have previously investigated the complexing of molybdate with 8-hydroxyquinoline (oxine), a reaction which can be regarded as a model for substrate binding in xanthine oxidase. More recently the complexing of tungstate with oxine, and molybdate and tungstate with oxine-5-sulphonic acid have been investigated.[2] The reactions may be summarized by equation (1) (M = Mo or W), where over the pH range

$$MO_4^{2-} + H^+ + Hox \rightleftharpoons [MO_2(OH)_2(ox)]^- \quad (1)$$

7·5—9·8 investigated the diprotonated complexes $[MO_2(OH)_2(ox)]^-$ are predominant. Complexing occurs in each case by an addition process, with increase in co-ordination number from four to six.

Our original intention was to extend these studies to a consideration of the reaction between oxine and an octahedral molybdenum complex, and thus investigate what is, in effect, a ligand-substitution process. The complex trioxo(diethylenetriamine)molybdenum(VI) was chosen since it is easily prepared,[3] and its crystal and molecular structure in the solid state have been determined.[4] Moreover following pH titrations, Marzluff suggested [3] that all three nitrogens remain co-ordinated in solution. The experiments described below clearly indicate that MoO_3(dien) and the tungsten analogue are extensively hydrolysed to oxyanions, MO_4^{2-}, and protonated diethylenetriamine in aqueous solution. Experiments in the first four sections are concerned with the trioxo(diethylenetriamine)molybdenum(VI) complex.

Preliminary Investigations.—The complex MoO_3(dien) is very soluble in water giving colourless solutions of greater than 0·4M-concentration, and pH *ca.* 6·5. At pH < *ca.* 6 solutions are unstable and precipitation of polynuclear molybdate species occurs.[3] Most experiments in the present study were carried out at pH > 7·0. On addition of oxine to a 100-fold excess of MoO_3(dien) a yellow solution was formed ($\lambda_{max.} = 373$ nm). As the molar ratio of oxine to MoO_3(dien) approaches 1 : 1 a yellow solid was produced which analysed for the dioxinate, $MoO_2(ox)_2$ (see Experimental section).

Equilibrium Studies on the Complexing of Oxine with MoO_3(dien).—The equilibrium constant for the formation of an oxine complex in solutions of MoO_3(dien) at 25°, with $[NO_3^-] = 0{\cdot}20$M (Na/NH_4NO_3), was determined spectrophotometrically at the absorption maximum (373 nm) for the mono-substituted oxine complex. The pH of solutions was adjusted by additions of small amounts of 0·35M-ammonia. The hydrogen-ion concentration was varied from $1{\cdot}8 \times 10^{-9}$ to $1{\cdot}0 \times 10^{-8}$M, the concentration of molybdenum(VI) varied from 5×10^{-3} to 4×10^{-2}M, and the concentration of oxine kept constant at $3{\cdot}2 \times 10^{-4}$M. Values of the absorbance (OD) of such solutions have a strong dependence on the hydrogen-ion concentration, but are consistent with the formation of a 1 : 1 complex (Figure 1). The dissociation constant for the complex, K_C, is given by equation (2)

$$K_C = \frac{[H^+][Hox][Mo^{VI}]}{[C]} \quad (2)$$

where Hox denotes neutral oxine, Mo^{VI} the molybdenum

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[1] P. F. Knowles and H. Diebler, *Trans. Faraday Soc.*, 1968, **64**, 977.

[2] H. Diebler and R. E. Timms, *J. Chem. Soc.* (*A*), 1971, 273.

[3] W. F. Marzluff, *Inorg. Chem.*, 1964, **3**, 395.

[4] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

not complexed to oxine, and C the oxine complex formed. Assuming (2) is valid and that a 1 : 1 complex is formed relation (3) can be derived. In this equation

$$\frac{1}{\mathrm{OD}-\mathrm{OD}_0}=\frac{1}{\Delta\mathrm{OD}}=\frac{1}{(\varepsilon_{\mathrm{C}}-\varepsilon_{\mathrm{Hox}})([\mathrm{Hox}]+[\mathrm{C}])}\left\{1+\frac{K_{\mathrm{C}}}{[\mathrm{H}^+][\mathrm{Mo}^{\mathrm{VI}}]}\right\} \quad (3)$$

OD_0 is the absorbance of the oxine in the absence of molybdenum(VI) and ε_C and ε_{Hox} are absorption coefficients for C and Hox. Thus by plotting $(\Delta OD)^{-1}$

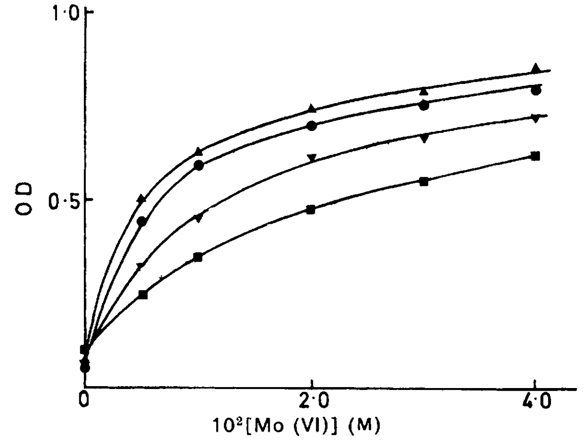

FIGURE 1 Dependence of absorbance (OD) in 1-cm cell on $[Mo^{VI}]$ and pH for solutions of MoO_3(dien) containing $3{\cdot}2 \times 10^{-4}$M oxine at 25°, $\lambda = 373$ nm, ▲ pH 7·99, ● pH 8·17, ▼ pH 8·38, ■ pH 8·74 (*cf.* Figure 1, ref. 1)

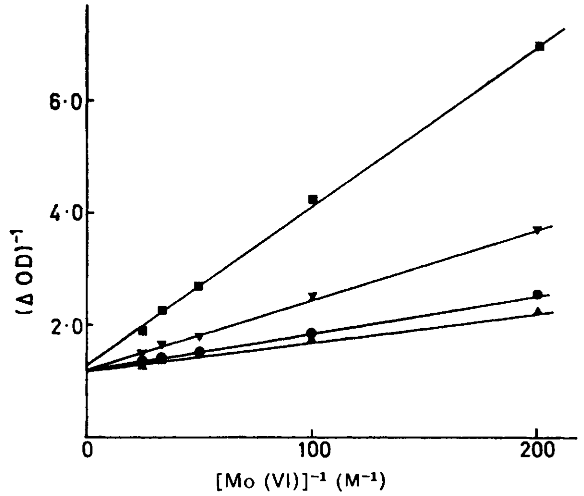

FIGURE 2 Dependence of $1/\Delta OD$ on $[Mo^{VI}]^{-1}$, $\lambda = 373$ nm, and pH for solution of MoO_3(dien) containing $3{\cdot}2 \times 10^{-4}$M-oxine at 25°. ▲ pH 7·99, ● pH 8·17, ▼ pH 8·38, ■ pH 8·74

against $[Mo(VI)]^{-1}$ at constant pH (Figure 2) both K_C and ε_C can be evaluated (Table 1), where ε_{Hox} is pH dependent due to the formation of small amounts of unprotonated (and uncomplexed) oxine at the higher pH values. Values of K_C were obtained at each pH using a standard unweighted least-squares programme and were then averaged to give $K_C = 4{\cdot}32 \pm 0{\cdot}20 \times 10^{-11}$ mol² l⁻². This value is quite close to that observed for the complexing of molybdate with oxine[1] (see Table 2). The value of K_C is modified by allowing for the activity coefficient of the hydrogen ion, which has previously been assumed to be 0·8 under similar conditions.* This correction allows the value of K_C obtained in the present study to be compared with that reported for the reaction of molybdate with oxine.[1] Absorption coefficients, ε_C, obtained in the two studies are also compared, Table 2.

TABLE 1

Dependence of K_C and ε_C on pH at 25°, for the complexing of oxine with MoO_3(dien) (supposed) in 0·2M-nitrate solution.

$10^9[H^+]$	$10^{11}K_C$ (mol² l⁻²)	$10^{-3}\varepsilon_C$ (l mol⁻¹ cm⁻¹)
10·15	4·69 ± 0·40	2·84
6·79	3·95 ± 0·25	2·81
4·17	4·46 ± 0·30	2·80
1·84	4·17 ± 0·30	2·80
Average	4·32 ± 0·20	2·81

Assuming activity coefficient of H⁺ in 0·2M nitrate medium is 0·8,[1] corrected value of $K_C = 5{\cdot}40 \pm 0{\cdot}25 \times 10^{-11}$ mol² l⁻².

TABLE 2

Comparison of K_C, ε_C, τ for the reactions of MoO_4^{2-} and MoO_3(dien) (supposed) with oxine in 0·2M-nitrate solution at 25°

	MoO_4^{2-} + oxine [a]	MoO_3(dien) + oxine
K_C (mol² l⁻²)	$4{\cdot}4 \pm 0{\cdot}4 \times 10^{-11}$	$5{\cdot}4 \pm 0{\cdot}25 \times 10^{-11}$
$\lambda_{max.}$ (nm)	372	373
ε_C(l mol⁻¹ cm⁻¹)	$3{\cdot}2 \times 10^3$	$2{\cdot}8 \times 10^3$
τ (ms) [pH 8·18 ± 0·01]	27·9	35·2
τ (ms) [pH 8·48 ± 0·01]	34·0	43·6

[a] From data in ref. 1.

Kinetic Studies on the Complexing of Oxine with MoO_3(dien).—The temperature-jump relaxation technique was used.[5] The relaxation was studied at 373 nm on a single-beam apparatus using a Xenon lamp. The reaction mixture was thermostatted at 22·4° before a jump of 2·6°. Experiments were carried out at pH 8·18 and 8·48 with $[MoO_3(dien)] = 4 \times 10^{-2}$M, [oxine] $= 4 \times 10^{-4}$M, and with $[NO_3^-] = 0{\cdot}2$M (Na/NH_4NO_3). Relaxation times, τ (Table 2), are compared with those calculated from data for the reaction of molybdate with oxine.[1]

TABLE 3

Molar conductivities (mmho) of aqueous solutions of sodium molybdate and trioxo(diethylenetriamine)-molybdenum(VI) at room temperature

Mo^{VI} concentration	2×10^{-3}M	2×10^{-1}M
Solution of $Na_2MoO_4,2H_2O$	233	150
Solution of MoO_3(dien)	197	95

Conductivity Measurements.—Conductivity measurements on the MoO_3(dien) complex in water at room temperature showed a high molar conductivity (Table 3),

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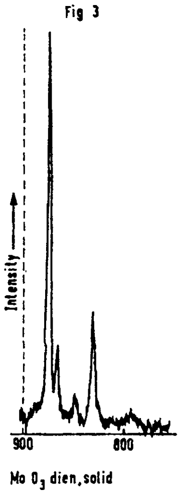
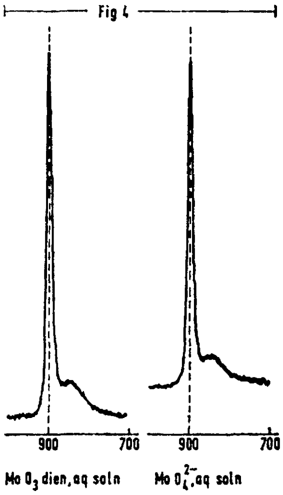
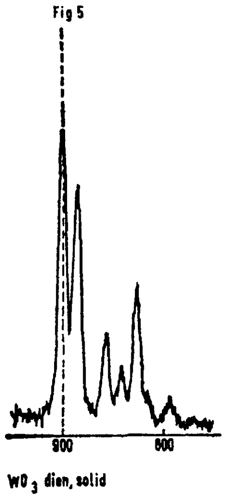
* A lower activity coefficient for the hydrogen ion would not be unreasonable; a value of 0·8 is used to enable comparisons with earlier work (ref. 1).

[5] M. Eigen and L. DeMaeyer in *Techniques of Organic Chemistry*, ed. Friess, Lewis, and Weissberger, Interscience, N.Y., 1963, VIII, pt. 2, p. 895.

and although this was somewhat less than that for sodium molybdate, considerable ionization was indicated.







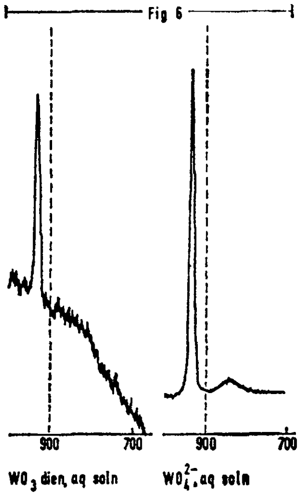


FIGURE 3 Raman spectrum (cm^{-1}) of solid MoO$_3$(dien)

FIGURE 4 Raman spectra (cm^{-1}) of *ca.* 0·2M-aqueous solutions of MoO$_3$(dien) and Na$_2$MoO$_4$

FIGURE 5 Raman spectrum (cm^{-1}) of solid WO$_3$(dien)

FIGURE 6 Raman spectra (cm^{-1}) of WO$_3$(dien) in water with excess diethylenetriamine, and of Na$_2$WO$_4$ in water

TABLE 4

Infrared and Raman vibrational frequencies (cm^{-1})[a]

Compound		ν(M–O)$_{sym}$	ν(M–O)$_{asym}$	δ(OMO)	Other bands	Reference
MoO$_3$(dien)	R solid	874(100)	830(30)[b]	378(3) 352(8) 336(3)	848(5),[b] 866(15)[b] 792(3),[b] 252(5) 240(5)	This work
	R solid	871(100)	826(30)	359(10)		7
	IR solid	878m[b]	839s	350m 369w 381m	887w, 898m 787w, 640m[c]	This work
	IR solid	876s[d,e]	825vs	380s		7
	R aq	892(100)	845(10)sh	318(13)		This work
	R aq	892(100)	839(30)	317(70)		7
	IR aq	898	Obscured			7
Na$_2$MoO$_4$,2H$_2$O	R solid	898(100)	840(15)		804(4)	This work
	R solid	897vs	843m	325m	836m, 805m	6
	R aq	897(100)	845(10)	320(13)		This work
	R aq	897vs	841m	318s		6
WO$_3$(dien)	R solid	902(100)	828(40)[b]	355(20)	888(80),[b] 858(20)[b] 843(10),[b] 795(5)[b]	This work
	IR solid	903m[b]	833s	343m 351m 360w 368vw	882,[b] 790m[b]	This work
	R aq	928	[f]	325[g]		This work
Na$_2$WO$_4$,2H$_2$O	R solid	929(100)	837(15)	340(30)	884(5)	This work
	R solid	935(100)	838(6)	325(9)		This work
	R aq	931vs	838m	335m	893w	6

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Raman intensities in brackets, scale 0—100 and relative to the strongest band. [b] Tentative assignment based on expected coincidence of Raman and i.r. bands. Some bands may belong to dien vibrations. [c] Bands above 900 cm^{-1} due to dien not reported. [d] Griffith and Wickins [7] do not report any dien frequencies. [e] Marzluff [3] gives bands at 876, 886, and 898 cm^{-1}. [f] Position uncertain because of fluorescence. [g] Broad band just discernible against the baseline which is rising steeply because of fluorescence.

Preparation of WO$_3$(dien).—A tungsten compound analysing for WO$_3$(dien) was prepared from tungsten trioxide and diethylenetriamine as described in the Experimental section. Attempts to isolate a chromium(VI) analogue or identify such a species in solution by visible-range spectroscopy were unsuccessful. Although the tungsten diethylenetriamine complex has been studied less extensively it was found to exhibit similar properties to the molybdenum complex. I.r. and Raman studies as reported in the next section are the best means of illustrating this similarity.

Raman and I.r. Studies on MoO$_3$(dien) *and* WO$_3$(dien).—Raman spectra of solids and *ca.* 0·2M-solutions were recorded over the range 1000—100 cm^{-1}. The most

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[6] R. H. Busey and O. L. Keller, jun., *J. Chem. Phys.*, 1964, **41**, 215.

[7] W. P. Griffiths and T. D. Wickins, *J. Chem. Soc.* (*A*), 1968, 400.

significant region containing the symmetrical and assymmetrical metal–oxygen stretching frequencies, is 900—800 cm^{-1}. The assignment of bending modes in the 400—300 cm^{-1} region is less certain.[6] The Raman spectrum of MoO_3(dien) is shown in Figures 3 and 4, and that of sodium molybdate in Figure 4. The solution spectrum of MoO_3(dien) is independent of pH over the range 6·2—8·5, and of added diethylenetriamine (pH *ca.* 11) up to a molar excess of 5 : 1 (*ca.* 1M-diethylenetriamine). Raman spectra of solid WO_3(dien) and of aqueous solution of WO_3(dien) and WO_4^{2-} are shown in Figures 5 and 6. Solutions of WO_3(dien) in water with excess of diethylenetriamine fluoresce.

I.r. spectra of MoO_3(dien) and WO_3(dien) were also determined. Details are shown alongside Raman data in Table 4. Information listed in earlier studies[3,7] is also given in Table 4. The i.r. assignments are based on the expected coincidence of Raman and i.r. frequencies.

DISCUSSION

The hydrogen-ion dependence of the equilibrium constant K_C, equation (2), is the same as that observed previously for the reaction of molybdate with oxine.[1,2] Furthermore the close agreement (*ca.* 20%) of data obtained from equilibrium and kinetic studies on the reactions of oxine with MoO_4^{2-} and MoO_3(dien) respectively suggests that the state of the molybdenum in both is similar. The crystal structure of MoO_3(dien) (ref. 4) indicates a *fac*-arrangement of the three oxo-ligands with distortion towards a tetrahedral configuration, $N\text{–}\widehat{Mo}\text{–}N$ averaging *ca.* 75°, and $O\text{–}\widehat{Mo}\text{–}O$ averaging 106°. It is possible that the complex should be regarded as pseudo-tetrahedral, and that it might therefore resemble MoO_4^{2-} chemically. However the form of the equilibrium constant for complexing with oxine, equation (2), suggests that no ligands dissociate since only one proton is consumed in the forward reaction. Despite previous conclusions that the diethylenetriamine is co-ordinated through three nitrogens, one possibility is that two of these are (initially) free and protonated. An equilibrium of the form (4) is thus possible.

$$[MoO_3(dienH_2)]^{2+} + H^+ + Hox \rightleftharpoons [MoO(OH)_2(ox)(dienH_2)]^{3+} \quad (4)$$

The extensive formation of $[MoO_3(dienH_2)]^{2+}$ clearly requires there to be a significant change in pH on dissolution of 0·2M-MoO_3(dien) in water. Little change in pH is observed, and yet conductivity measurements indicate considerable ionization. We consider, therefore, the alternative of almost complete dissociation [equation (5)] to be more probable. Protonation of diethylenetriamine is extensive below pH 10,[8] and since under the conditions used the stable form of the ligand will be doubly protonated, it can be seen that the equilibrium in (5) involves no significant change in pH. It is not surprising therefore that from pH measurements alone Marzluff[3] concluded that the diethylenetriamine remained co-ordinated and is tridentate in aqueous solution. Equation (5) readily explains the precipitation of sodium molybdate when sodium hydroxide and ethanol are added to a solution of MoO_3(dien). The lower conductivities of solutions of MoO_3(dien) as compared to sodium molybdate can be accounted for by the different behaviour often observed for bi-bi and uni-bi electrolytes.[9] Some degree of association between the species MoO_4^{2-} and $dienH_2^{2+}$ is possible.

$$MoO_3(dien) + H_2O \rightleftharpoons MoO_4^{2-} + dienH_2^{2+} \quad (5)$$

It is, of course, surprising that MoO_3(dien) should be precipitated almost quantitatively on addition of ethanol to a solution of MoO_3 and diethylenetriamine. This suggests that the equilibration in (4) is extremely rapid. The difference in equilibrium constants for the formation of the oxine complex, Table 2, is not in the direction expected for it to be indicative of undissociated MoO_3(dien). Since in the present study, the ionic strength will vary with concentration of molybdenum(VI) if MoO_3(dien) is hydrolysed, equation (5), this could account for the higher K_C value. Thus with $[Mo^{VI}] = 0{\cdot}005M$ it can be shown that $\mu = 0{\cdot}22M$, and with $[Mo^{VI}] = 0{\cdot}04M$, $\mu = 0{\cdot}36M$. This may be the reason for all determinations with $[Mo^{VI}] = 0{\cdot}04M$ giving higher absorbance readings than expected, Table 2.

The Raman and i.r. studies on the MoO_3(dien) complex substantiate the above arguments. Marzluff[3] has discussed the i.r. spectrum of MoO_3(dien) solid. Griffiths and Wickins[7] have reported details of i.r. and Raman studies on the solid and on saturated aqueous solutions of MoO_3(dien), but have not commented on certain important features of these spectra. We note for example that solid and aqueous Raman spectra of MoO_3(dien) differ significantly. Also Raman spectra for MoO_3(dien) and sodium molybdate in aqueous solution, Figure 4, closely resemble each other in the ν(Mo–O) and δ(Mo–O) regions. No bands attributable to diethylenetriamine co-ordinated or unco-ordinated are observed in the solution Raman spectra, although it is likely that some of the bands in the Raman spectra of the solids, Figures 3 and 5, are due to vibrations of the complexed ligand.

To summarize, the evidence presented here points to extensive hydrolysis of MoO_3(dien) to MoO_4^{2-} and diethylenetriamine, which at pH < 10 is protonated.[8] The complex WO_3(dien) has been prepared and found to behave in a similar manner. Further evidence for the unusual behaviour of MoO_3(dien) is that it is insoluble in all the following solvents: methanol, ethanol, propan-2-ol, n-hexanol, dimethyl sulphoxide, diethyl ether, light petroleum, carbon tetrachloride, chloroform,

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[8] G. H. McIntyre, jun., B. P. Block, and W. C. Fernelius, *J. Amer. Chem. Soc.*, 1959, **81**, 529.

[9] See for example, C. G. Monk, ' Electrolytic Dissociation,' Physical Chemistry Series, ed. E. Hutchinson and P. Van Rysselberghe, Academic Press, New York, vol. VIII, 1962, p. 132.

dimethylformamide, acetone, dioxan, benzene, toluene, and n-pentane.* Water containing up to 50% ethanol appears to be the only solvent in which the complex dissolves. Hydrolysis as in equation (5) is largely responsible for the solubility in this medium.

EXPERIMENTAL

Preparation of Trioxo(diethylenetriamine)molybdenum(VI).—A sample of MoO_3(dien) was prepared from molybdenum trioxide (AnalaR grade) and diethylenetriamine (Reagent grade) as described in ref. 3. (Found: C, 19·4; N, 17·0; H, 5·2. Calc. for $MoC_4H_{13}O_3N_3$: C, 19·4; N, 17·0; H, 5·3%).

Attempts to prepare MoO_3(dien) from either MoO_3 in the presence of sodium ions, or from sodium molybdate, were unsuccessful, and addition of these solutions to ethanol yielded hydrated sodium molybdate (Found: H, 1·8; $C < 0·2$. Calc. for $Na_2MoO_4,2H_2O$: H, 1·6; C, 0·0%. The i.r. spectrum of the solid was also identical to that of sodium molybdate.

Preparation of Trioxo(diethylenetriamine)tungsten(VI).—The method used is a modification of that for the preparation of MoO_3(dien). However a larger excess of diethylenetriamine was required to prevent precipitation of tungsten oxide. Diethylenetriamine was also added during recrystallization.

AnalaR grade tungsten trioxide (0·02 mol, 4·6 g), was added to a solution of diethylenetriamine (0·1 mol, 10·3 g) in water (100 ml). The mixture was boiled until all the yellow oxide had dissolved. The solution was then filtered to remove small amounts of the non-stoicheiometric ' blue ' oxide, diluted with water (10 ml) to allow for evaporation losses, and then cooled; 25 ml was added slowly with stirring to absolute ethanol (250 ml). The white solid produced, was filtered, washed with ethanol, and dried. Recrystallization was achieved by dissolving the solid in water (25 ml) containing diethylenetriamine (1·0 g); the product was filtered off, washed with ethanol, and dried by suction; yield from 4·6 g of tungsten trioxide was 4·8 g (70%) (Found: C, 14·3; H, 3·85; N, 12·5. Calc. for $C_4H_{13}N_3O_3W$: C, 14·35; N, 12·55; H, 3·9%).

Attempted Preparation of Trioxo(diethylenetriamine)chromium(VI).—We were unable to isolate or identify the chromium(VI) complex, CrO_3(dien), under conditions similar to those used for the preparation of the molybdenum and tungsten complexes. Addition of aqueous solution of CrO_3 and diethylenetriamine to an excess of ethanol produced, initially, a yellow solid which changed rapidly to a yellow-orange oil. This was possibly due to oxidation of diethylenetriamine by chromium(VI).

The complex does not seem to exist in aqueous solution even in the presence of a 100-fold excess of diethylenetriamine. For example chromium trioxide ($1·3 \times 10^{-3}$M) in diethylenetriamine (0·09M) and in sodium hydroxide (1·0M) have identical spectra [$\lambda_{max.}$ 371 nm ($\varepsilon_{max.}$ $4·22 \times 10^3$ l mol^{-1} cm^{-1})]. The pH of these solutions is close to 12, and at this pH CrO_4^{2-} is the only oxochromium(VI) species present.[10]

Attempts to isolate a molybdenum oxine complex with diethylenetriamine still bonded were unsuccessful. To a solution of trioxodienmolybdenum(VI) (1·0 g) in water (50 ml), oxine (0·6 g) (molar ratio 1 : 1) was added slowly with stirring and heating. The solution became yellow, and a yellow precipitate formed. This was collected and analysed (Found: C, 52·5; H, 3·0. Calc. for $C_{18}H_{12}MoN_2O_4$: C, 51·9; H, 2·9%). Addition of nitrate to the filtrate produced a creamy yellow solid which was also collected (Found: C, 50·3; H, 2·75. Calc. for $C_{18}H_{12}MoN_2O_4$: C, 51·9; H, 2·9%); both solids analysed for $[MoO_2(ox)_2]$.

A radiometer 4A pH meter with a radiometer G.202B glass electrode and K401 calomel electrode were used. The pH meter was standardized using buffer of pH 6·5 ± 0·02 (20°). Conductivity measurements were on a Radiometer type CDM 2D conductivity meter with direct readout. A Radiometer CDC 104 (GL) conductivity cell was used. Raman spectra were recorded on a Coderg PHO spectrometer using argon and helium–neon lasers for excitation. I.r. spectra (KBr discs and Nujol mulls) were obtained on a Perkin-Elmer 457 instrument. Both i.r. and Raman spectra are accurate to ± 2 cm^{-1}.

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* We cannot rule out the possibility that in some cases at least the complex dissociates, the diethylenetriamine dissolves, and insoluble MoO_3 remains.

[10] Y. Sasaki, *Acta Chem. Scand.*, 1962, **16**, 719.