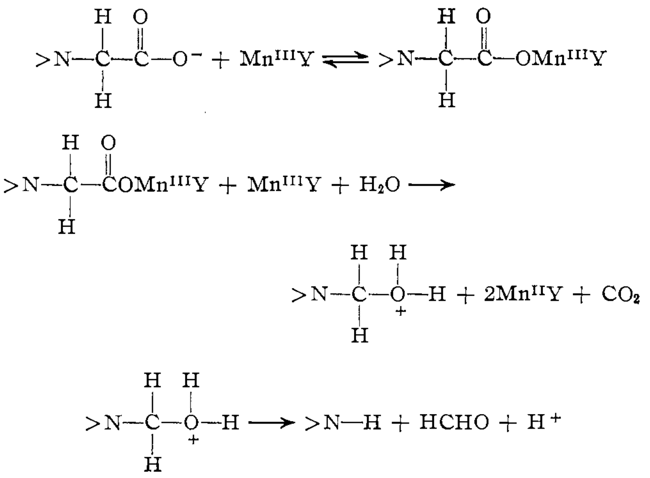
formaldehyde produced two moles of complex had been consumed.

These results also indicated that the same products resulted from each of the three parallel parts of the rate expression. Terms one and three of eq. 5 involve only the difference in the ease with which $Mn^{III}Y$ can oxidize the free EDTA. Term two of eq. 5 must involve the possibility of intramolecular electron transfer from the chelated EDTA to the manganese(III). This process is much slower than either of the other processes, but becomes the rate-controlling process when the free EDTA concentration becomes very small.

A mechanism which is in agreement with the experimental data is shown.



$$>N-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-O^- + Mn^{III}Y \rightleftharpoons >N-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-OMn^{III}Y$$

$$>N-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}OMn^{III}Y + Mn^{III}Y + H_2O \longrightarrow >N-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{+}{O}}}-H + 2Mn^{II}Y + CO_2$$

$$>N-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{+}{O}}}-H \longrightarrow >N-H + HCHO + H^+$$

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Polyamine Complexes of Molybdenum Trioxide

BY W. F. MARZLUFF

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Diethylenetriamine (dien) forms a crystalline, monomeric complex with MoO_3 having the formula (dien)MoO_3. Ethylenediamine and triethylenetetramine dissolve MoO_3, but compounds of uniform composition could not be obtained. Partial neutralization of these solutions results in precipitation of photosensitive complex mixtures of amine salts of molybdates. The variation of precipitation and neutralization points with the amine used is employed to predict possible structures for these complexes in solution.

Introduction

No report of a true crystalline amine complex, as differentiated from a salt, of molybdenum(VI) has been found in the literature. Lower valence states of molybdenum have been studied, and molybdenum(V) chloride forms a 1:1 adduct with trimethyl- and triethylamine.[1] Molybdenum(0) also forms complexes with amines, a most interesting one with regard to this paper being (diethylenetriamine)$Mo(CO)_3$.[2]

The reactions between solid molybdenum trioxide, MoO_3, and several polyamines have now been investigated. We have found that MoO_3 forms a monomeric, crystalline, 1:1 compound with diethylenetriamine (dien) and that more complex materials are formed with ethylenediamine (en) and triethylenetetramine (trien).

Experimental

(dien)MoO_3.—Reagent grade molybdenum trioxide (7.2 g., 0.05 mole) was suspended in a solution of dien (10.3 g., 0.10 mole) in 200 ml. of H_2O, and the mixture was heated to boiling on a hot plate with stirring until the solids were all dissolved. The pale yellow solution was cooled, diluted to 250 ml., and a 50-ml. aliquot was added to 300 ml. of rapidly stirred ethanol. The resulting white solid was filtered, washed with ethanol, redissolved in 50 ml. of de-ionized water, and reprecipitated with ethanol. The product separated in small, white needles and weighed 2.3 g., a yield of 94%. Larger crystals can be obtained by dissolving about 2 g. of the complex in 30–40 ml. of water, adding ethanol until the solution is turbid, and cooling in an ice bath.

Anal. Calcd. for $C_4H_{13}N_3O_3Mo$: C, 19.4; H, 5.3; N, 17.0; mol. wt., 247. Found: C, 19.3; H, 5.6; N, 16.8; mol. wt. in H_2O, 290.

Titration Experiments.—Titrations were carried out using a Beckman Model G pH meter. The results were independent of the acids used (HCl, H_2SO_4, $HClO_4$), and the acid anions did not appear in the solid products isolated at the end points in the titrations.

Anal. From (dien)MoO_3 titration: C, 7.6; H, 2.9; N, 6.3; Mo, 54; N/Mo, 1.2. From (trien)MoO_3 titration: C, 8.5; H, 2.7; N, 7.2; Mo, 53; N/Mo, 1.1. From en-MoO_3 titration: C, 4.9; H, 2.8; N, 5.7; Mo, 56; N/Mo, 0.7.

Molybdenum was determined by digesting the sample with aqua regia for several hours, heating with hydrochloric acid to remove the nitric acid, diluting to volume, and estimating the molybdenum according to the colorimetric method of Busev and Fan[3] using thioglycolic acid.

Results and Discussion

Aqueous solutions of en, dien, and trien will dissolve considerable quantities of solid MoO_3 up to a ratio of nitrogen to molybdenum of 2.2 to 2.5. Concentrations of MoO_3 exceeding 25% by weight can be readily obtained free of other metal ions. Such solutions have a pH between 6 and 7. By contrast, solutions of am-

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(1) G. A. Edwards and G. W. A. Fowles, *J. Chem. Soc.*, 24 (1961).

(2) E. W. Abel, M. A. Bennett, and G. A. Wilkinson, *ibid.*, 2323 (1959).

(3) A. I. Busev and C. Fan, *Z. anal. Chem.*, **193**, 153 (1963).

monium molybdate of similar concentrations and nitrogen to molybdenum ratios have a pH of 8–9.[4]

(dien)MoO_3.—From an equimolar solution of dien and MoO_3 a white, crystalline compound can be precipitated with ethanol. The elemental analysis clearly shows the stoichiometry to be (dien)MoO_3 with no solvent molecules of crystallization. The complex is very soluble in water but insoluble in organic solvents. The detailed X-ray analysis of the structure is being reported in this issue by Cotton and Elder,[5] who find the complex to be monomeric with all three amine nitrogen atoms coordinated to octahedral molybdenum in the *cis* configuration. The three oxygen atoms are equivalent and doubly bonded to the molybdenum.[5]

The infrared spectrum of the complex has several interesting features. The N–H bands at 3240 (s) and 3120 (s) $cm.^{-1}$ are characteristic of amines but are lowered from their usual values, indicating strong hydrogen bonding. There is also a broad, weak band with multiple fine structure centered at 2250 $cm.^{-1}$ attributed to a combination of the observed NH_2 deformation at 1606 $cm.^{-1}$ and NH_2 wag and/or twist not directly observed but expected in the neighborhood of 600 $cm.^{-1}$. A similar band is observed in liquid water at 2200 $cm.^{-1}$, where a similar hydrogen bonding situation exists. There is also a very strong molybdenum–oxygen stretching band at 835 $cm.^{-1}$. One would expect to find more than one molybdenum–oxygen stretching frequency [analogous to the carbonyl frequencies in (dien)$Mo(CO)_3$],[2] but there are no other strong bands in this region of the spectrum. One of three weak bands (876, 886, 898 $cm.^{-1}$) might be thus assigned, but they could also be ligand bands. Comparison with the spectrum of (dien)$Mo(CO)_3$ does not allow an unequivocal assignment of the ligand bands. This figure of 835 $cm.^{-1}$ is unusually low for a monomeric complex and far removed from the position for unbridged molybdenum–oxygen bonds at about 940 $cm.^{-1}$. Mo=O bonds arbitrarily have been assigned frequencies above 900 $cm.^{-1}$ and bridging Mo–O–Mo systems frequencies below this figure.[6] We suggest that the strong hydrogen bonding of the amine hydrogen atoms to the oxygen atoms has caused this displacement and perhaps even lengthened the Mo=O bond. This result makes it difficult to assess the kind of molybdenum–oxygen bonding existing in compounds whose detailed structure is not known. Probably these considerations should be applied to other metal–oxygen systems as well.

en–MoO_3 and trien–MoO_3 Complexes.—Contrary to the above result, no discrete, crystalline compounds of en and trien with MoO_3 have been precipitated from solution. Solids are obtained which have variable composition and which cannot be redissolved completely in water. Their infrared spectra contain up to four strong bands in the 830–930 $cm.^{-1}$ region, similar to polymolybdates.

Titration of Complexes.—Acid titration of solutions of MoO_3 in aqueous polyamines produced infusible, insoluble solids of indefinite stoichiometry (see Experimental section).

The pertinent facts from these titrations are given in Table I. The results are independent of the acid used, and the acid anion does not appear in the solids isolated. Two conclusions can be drawn from these data. A comparison of the initial N : Mo ratios with the initial pH of the solutions indicates that no more than three nitrogen atoms are associated with each molybdenum atom in solution. Secondly, when a complex containing dien and trien achieves a net double positive charge, it dissociates sufficiently to permit formation and precipitation of polymolybdates.

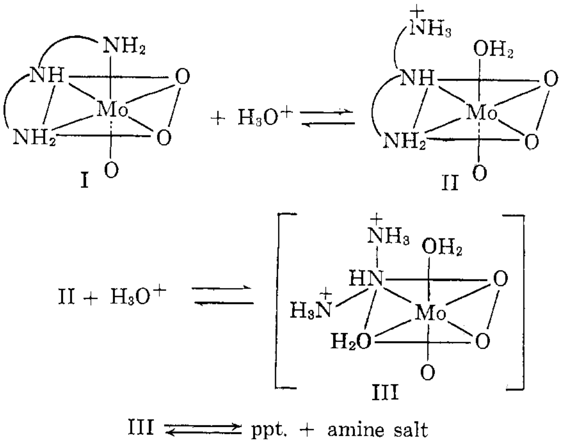
Table I

Titration of Aqueous Polyamine Solutions of MoO_3

Expt.	Amine	Ratio N:Mo[a]	Ratio H^+:N Cloud break point		Ratio H^+:Mo Cloud break point		pH		
							Initial	cloud	break point
1	dien	3.0	0.0	0.68	0.0	2.04	6.1	6.0	4.5
2	trien	4.0	0.21	0.55	0.84	2.20	8.1	5.9	4.5

[a] Initial $[MoO_3]$ = 5×10^{-2} *M*.

The titration data presented in Table I can perhaps best be explained by a series of successive protonations of amino groups. In the case of the (dien)MoO_3 complex, when a small amount of acid is added, the following steps can occur.



The relative proportions of II and III are governed by the difference in p*K* values of the two terminal amine groups. At the end point of the titration, the solution contains 67% of the amine as the free salt, virtually no molybdenum, and two equivalents of acid have been added per dien. From the infrared spectrum of the solid precipitate, the amine groups in the solid are all present as amine salts, and there are three strong bands in the metal–oxygen region (935, 900, 850 $cm.^{-1}$).

Similar titration behavior is displayed by the trien–MoO_3 solutions. Here, however, the higher pH of the solution (8.1) indicates that only three of the four amino groups are coordinated to molybdenum. As with (dien)MoO_3, when two amino groups are neutralized, precipitation is complete. The single uncoordinated amino group, being much more basic

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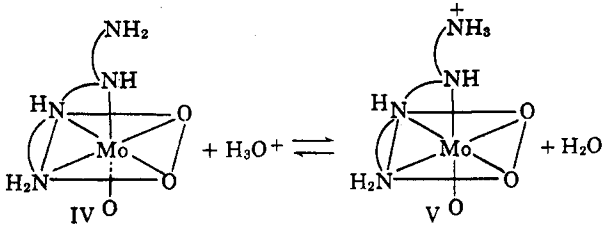
(4) Z. G. Karov and F. M. Perel'man, *Zh. Neorgan. Khim.*, **5**, 343 (1960).

(5) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

(6) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 3552 (1959).

than those attached to the molybdenum, is, therefore, initially protonated on addition of acid as shown below and in Table I, expt. 2.



Furthermore, the data suggest that no other amino group is protonated until the conversion of IV to V is nearly complete. At this point some protonation of one of the coordinated amino groups occurs, and solid begins to form. Precipitation again is complete when two of the four amino groups have been neutralized.

Acknowledgment.—The author is indebted to Mr. N. B. Colthup for the interpretation of the infrared spectra.

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The Crystal and Molecular Structure of Trioxo(diethylenetriamine)molybdenum(VI)[1a]

BY F. A. COTTON[1b] AND R. C. ELDER[1c]

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The crystal and molecular structure of MoO_3·dien (dien = diethylenetriamine) has been determined with high accuracy (final residual, 0.058) using single crystal diffraction data gathered with a counter diffractometer. The molecules contain molybdenum atoms coordinated in a distorted octahedron by three mutually *cis* oxygen atoms at an average distance of 1.736 Å. and three nitrogen atoms at an average distance of 2.324 Å. The N–Mo–N angles average ~75°, while the O–Mo–O angles average about 106°. The chelate rings are puckered in the expected manner. Intermolecular hydrogen bonding is extensive. Approximate positions (±0.1 Å.) for the hydrogen atoms obtained from a Fourier difference synthesis are also reported.

Introduction

The structural chemistry of molybdenum complexes is not well known, but it appears likely to be interesting and worthy of study from a purely chemical point of view. Thus, for example, molybdenum in its higher oxidation states forms a number of compounds containing MoO groups, and information on these would presumably be useful in understanding the behavior of MO groups generally. An added stimulus is provided by the occurrence of molybdenum in various enzymes concerned with nitrogen metabolism and, perchance, with *in vivo* nitrogen fixation. In these enzymes, it appears that the molybdenum is operative in the V state, but perhaps present in both the V and VI states.[2]

In addition to studying some compounds prepared in this laboratory, we have examined the new and rather novel compound MoO_3·trien, trioxo(diethylenetriamine)molybdenum(VI), discovered by Dr. William Marzluff.[3] The complete molecular and crystal structure determination by X-ray methods is reported and discussed in this paper.

Experimental

The crystals supplied were beautifully developed rectangular parallelepipeds, white in color. Precession photographs showed the unit cell to be orthorhombic. The cell edges, measured with the precession camera and the single crystal orienter (*vide infra*), are a = 6.863 ± 0.008, b = 10.250 ± 0.007, c = 11.705 ± 0.005 Å. By the flotation technique, the density was found[3] to be 2.0 ± 0.1 g. cm.$^{-3}$. This indicates that there are four molecules per unit cell, since the calculated density is then 2.1 g. cm.$^{-3}$.

From precession photographs of the $0kl$, $1kl$, $2kl$, $hk0$, $hk1$, $hk2$, and $hk3$ zones, the following systematic absences were determined: $0kl$, $k \neq 2n$; and $h0l$, $l \neq 2n$. From this information the possible space groups[4] are $Pbc2_1$ (No. 29) and Pbcm (No. 57).

A crystal of approximate dimensions 0.2 × 0.2 × 0.5 mm. was mounted and oriented with the c-axis (the long dimension of the crystal) along the spindle on a General Electric single crystal orienter (Furnas-Harker eucentric goniometer). X-Rays (Mo Kα) were generated with a G.E. XRD-5 unit and scattered intensities recorded with a scintillation detector. Measurements of any given $00l$ reflection as the crystal was rotated about c revealed no variation greater than 5%, thus confirming that crystal geometry and dimensions limit variations in absorption (μ = 15 cm.$^{-1}$) sufficiently that absorption corrections may be neglected.

Intensity measurements were made by the moving crystal method of Furnas,[5] with the modification that background measurements were made at the lowest and highest 2θ of the scan without displacing the crystal. Each of the two background

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[1] (a) Supported by the National Institutes of Health; (b) Fellow of the Alfred P. Sloan Foundation; (c) N.I.H. Predoctoral Fellow.

[2] For an introductory review see R. J. P. Williams in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961.

[3] W. F. Marzluff, Central Research Laboratories, American Cyanamid Co., Stamford, Conn. Dr. Marzluff supplied the crystals used in this study. A communication describing the preparation and chemical characterization of the compound appears elsewhere in this journal: *Inorg. Chem.*, **3**, 395 (1964).

[4] "International Tables of Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952.

[5] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric X-Ray Department, 1957.