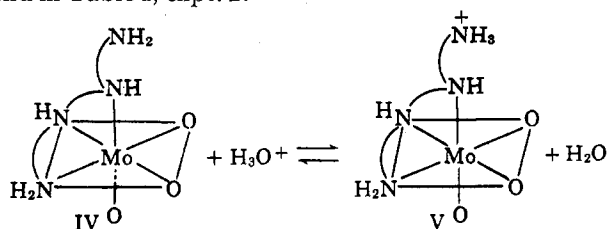


than those attached to the molybdenum, is, therefore, initially protonated on addition of acid as shown below and in Table I, expt. 2.



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.

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The Crystal and Molecular Structure of Trioxo(diethylenetriamine)molybdenum(VI)^{1a}

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The crystal and molecular structure of MoO₃·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 MoO₃·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 $a = 6.863 \pm 0.008$, $b = 10.250 \pm 0.007$, $c = 11.705 \pm 0.005$ Å. By the flotation technique, the density was found³ 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 groups⁴ are Pbc₂ (No. 29) and Pbcm (No. 57).

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.5$ 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 K α) 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 ($\mu = 15$ 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

(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.

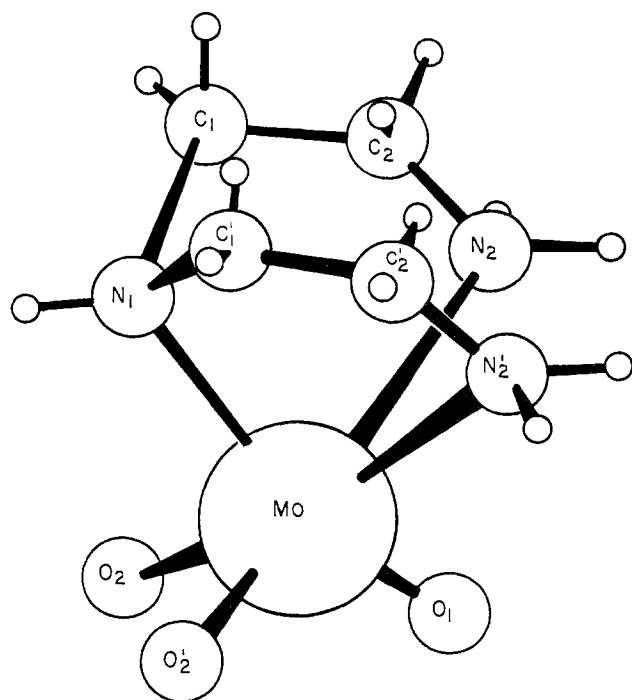


Fig. 1.—A perspective view of one molecule of $\text{MoO}_3 \cdot \text{dien}$. Atoms are numbered for reference in the tables.

measurements was for one-half the time of the scan and their sum was subtracted from the total of scan counts to give an observed intensity. The intensities for all the peaks were then normalized to the same scan rate and time scales. Each of the measurements was made twice in an effort to lessen statistical error and avoid operator error. The diffractometer was operated at a take-off angle of 2° , which gave a narrow source, to increase the accuracy of determination. Scans were performed over a range of 2.66° for $2\theta > 15^\circ$, to ensure that the total peak was scanned. For scans in the sphere $2\theta < 15^\circ$, some care was necessary to ensure that only the $K\alpha_1$ - $K\alpha_2$ doublet was measured and no radiation from neighboring reflections. In these cases, the scan width was reduced to 1° .

Once the orientation of the crystal on the goniometer had been established, Professor D. P. Shoemaker's 709/7090 program, GONIO-MIXG2, was used to compute settings for all reflections in the sphere $0 < 2\theta < 45^\circ$ and to determine simultaneously the reciprocal Lorentz and polarization factors. The output of this program was taken on cards which were then machine ordered, using a small auxiliary program written in Fortran, for efficiency in adjusting the goniometer. They were then printed in a format suitable for entering the scan and background readings as measured. The measured intensities were then punched on the cards and these returned to the computer to obtain $|F|^2$ and $|F|$ values.

Structure Determination

A three-dimensional Patterson function of one octant was computed; the huge Mo-Mo vector was immediately obvious at $0.133, \sim 0.05, 1/2$. The nonzero value of Y is crucial and was established with certainty by calculating the Patterson function on a very fine grid (units of $b/120$); although the actual value (0.05) is not very precise (the final coordinates show that it should be 0.0396), the fact that it is nonzero appeared certain. On this basis, the space group $\text{Pbc}2_1$ was ruled out, as well as the $4c$ position for molybdenum in Pbcm . Since the formula unit cannot have a center

TABLE I

FRACTIONAL ATOMIC COORDINATES						
Atom	x/a	y/b	z/c	σ_a	σ_b	σ_c
Mo	0.0566	0.0002	0.0198	0.0001	0.2500	...
O ₁	.2227	.0015	.1476	.0009	.2500	...
O ₂	.1106	.0010	.9220	.0007	.3688	0.0006
N ₁	.7465	.0017	.9274	.0011	.2500	...
N ₂	.8696	.0012	.1396	.0008	.3733	.0007
C ₁	.6420	.0016	.9582	.0010	.3548	.0009
C ₂	.6610	.0015	.1041	.0012	.3877	.0011
H (N ₁)	.250033302500	...
H ₁ (N ₂)	.100060330333	...
H ₂ (N ₂)	.160074331033	...
H ₁ (C ₁)	.283041330800	...
H ₂ (C ₁)	.416608334266	...
H ₁ (C ₂)	.310010660000	...
H ₂ (C ₂)	.400016001833	...

of symmetry, the $4a$ and $4b$ positions of Pbcm are also impossible, which leaves the $4d$ position, requiring molecular symmetry C_s , as the only possibility. The complete success of refinement to a very low residual, described below, shows that this conclusion is correct.

With the molybdenum atom at 0.0666, 0.0250, 0.2500, it was found to contribute significantly to approximately two-thirds of the reflections. Signs based on the molybdenum contributions alone were given to these $|F_{\text{obsd}}|$ and a three-dimensional Fourier synthesis computed. An image of the molecule was clearly seen and an initial set of atom coordinates estimated. The y -coordinate of Mo was shifted to 0.017. A structure factor calculation, using all atoms except hydrogens, all observed reflections, and estimated isotropic temperature factors (1.0 \AA^2 for Mo; 3.0 \AA^2 for C and N) gave a residual, $R = (\sum |F_c| - |F_o|) / \sum |F_o|$, of 0.32. After three cycles of least squares refinement of the x and y molybdenum coordinates, an intuitive adjustment of the oxygen atom coordinates, three more cycles varying all adjustable heavy atom coordinates, and, finally, six cycles varying all adjustable positional parameters and isotropic temperature factors, the residual had dropped to 0.093. In all least-squares refinements, all reflections were assigned a weight of unity.

A difference Fourier synthesis was then computed. In addition to showing distinct peaks corresponding to the hydrogen atoms on N₂ and the carbon atoms, this showed marked indications of anisotropic motions by the heavier atoms. A cycle of least-squares refinement using anisotropic temperature parameters was run and this lowered the residual to 0.087. At this point, several reflections, for which agreement was still exceptionally poor, were assumed to have been affected by extinction or other random error and removed from further calculations. They are listed at the end of Table III. A second cycle of refinement with anisotropic temperature factors brought the residual down to 0.072.

Another difference Fourier synthesis was now calculated. There were now no indications of significant, unaccounted-for vibrational motions, but peaks assignable to hydrogen atoms were quite evident. For the six hydrogen atoms on N₂, C₁, and C₂ these peaks corresponded approximately to 0.5–0.8 electron. The peak

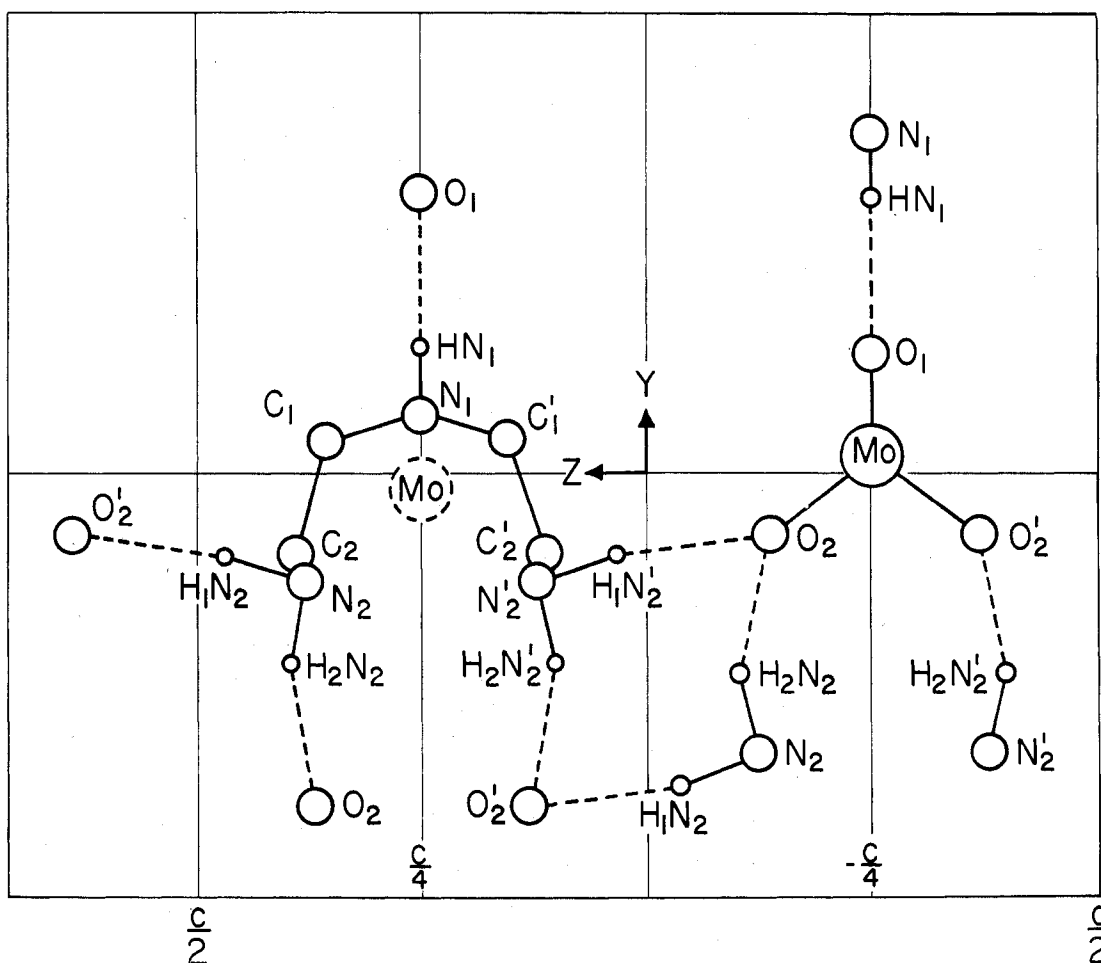


Fig. 2.—A projection of the structure from $x = 1/2$ to $x = 1$ on the (100) plane, to illustrate the hydrogen bonding.

TABLE II
ANISOTROPIC TEMPERATURE FACTORS^{a, b} $\times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	47.0 (2.5)	22.3 (1.1)	21.8 (0.8)	0.0	0.0	0.1 (0.4)
O ₁	40.8 (21.9)	25.2 (9.4)	56.1 (9.4)	0.0	0.0	19.5 (12.4)
O ₂	79.2 (16.4)	30.3 (6.8)	32.9 (6.2)	-24.7 (8.2)	3.2 (5.5)	7.0 (8.7)
N ₁	33.0 (25.3)	18.4 (11.0)	41.2 (10.4)	0.0	0.0	-20.1 (14.1)
N ₂	41.0 (17.1)	24.6 (7.6)	22.3 (6.3)	-1.9 (8.9)	3.6 (6.1)	5.5 (9.7)
C ₁	79.1 (22.5)	51.6 (10.9)	21.9 (8.3)	25.6 (11.8)	17.1 (7.9)	-7.2 (13.4)
C ₂	37.1 (20.7)	68.7 (12.1)	43.3 (9.5)	8.4 (12.3)	10.6 (9.0)	2.9 (13.9)

^a All hydrogen atoms were assigned an isotropic temperature factor, B , of 4.0 \AA^2 . ^b Standard deviations are given in parentheses.

for the hydrogen atom of N_1 was not well resolved and the coordinates selected for it are very uncertain, though plausible.

The hydrogen atoms were now introduced with isotropic temperature parameters, B , of 4.0 \AA^2 for each, and their coordinates and B values were kept fixed in further calculations. The next cycle of refinement reduced R to 0.060 and all changes in parameters were less than half the standard deviations. The parameters produced in this cycle are listed in Tables I and II. These parameters were used in a final structure factor calculation giving the F_c values recorded in Table III and producing a final residual of 0.058.

Discussion

From the positional parameters given in Table I, the interatomic distances and interbond angles given

in Tables IV and V were calculated. A perspective view of the molecule, with identifying numbers for the atoms, is shown in Fig. 1.

With regard to the components of the temperature factor tensors, it may first be noted that the standard deviations are quite large. It is unlikely that physical significance can be attached to most of these numbers. However, a few of the most marked features seem physically reasonable. Thus the O_1 atom apparently moves much more perpendicular to the mirror plane than in this plane; the in-plane motion is likely to be more restricted both by the hydrogen bond and by oxygen-oxygen repulsions. It also appears that the carbon atoms vibrate more out of the mean chelate ring planes than in them, as would certainly be expected.

TABLE III
OBSERVED AND CALCULATED STRUCTURE FACTORS

Table with columns for h, k, l, F0, Fc and multiple rows of numerical data representing observed and calculated structure factors.

Coordination of Molybdenum.—This appears to be the first structurally well-characterized example of a discrete molecular complex of Mo(VI). The molybdenum is six-coordinate, and the array of ligand atoms is roughly octahedral, but the distortions of such an ideal polyhedron are very considerable. The two O_1 -Mo- O_2 bond angles are 106.8° and the O_2 -Mo- O_2' bond angle is 105.3° , whereas the N-Mo-N angles are all well below 90° , namely, 73.1 , 73.1 , and 80.0° . Moreover, the molybdenum-ligand bond lengths are also very disparate, Mo-N bonds being 2.320 , 2.320 , and 2.332 Å., while the Mo-O bonds are 1.735 , 1.735 , and 1.739 Å. The Mo-N bonds are all of the same length within the standard deviations, as are the Mo-O bonds.

It seems likely that the variation in bond angles about molybdenum is largely due to the fact that the shortness of the Mo-O bonds tends to produce very short approaches of nonbonded oxygen atoms. This can be lessened by expanding the O-Mo-O angles at the expense of the N-Mo-N angles, which are between much longer bonds.

The Mo-O bond length can be compared with data for some other M-O bonds, but there are actually rather few such data available for bonds to second and third transition series elements. In the *trans*-[OsCl₄O₂]²⁻ ion,⁶ the Os-O distances are 1.75 ± 0.02 Å., while in ReClO₃, the Re-O bonds⁷ are 1.761 ± 0.003 Å. Thus the Mo-O distances observed here seem typical insofar as comparisons are possible. Probably in MoO₃·dien, as well as in the other two compounds, the M-O bonds may be considered to be approximately double bonds.

The Mo-N bonds are somewhat longer than we anticipated, something in the neighborhood of ~ 2.25 Å. being more in accord with the M-Cl distances in the two species mentioned above and in other molecules. However, the M-Cl bonds may have partial multiple character and the Mo-N bonds may tend to be longer than what would be expected for a normal, as opposed to a coordinate, single bond.

Chelate Ring Geometry.—Each of the five-membered rings is puckered in the manner expected both on theory⁸ and by analogy with previous experimental findings.⁹ The results may be conveniently expressed⁸ by considering a projection of the chelate ring down the C-C axis. The angle, θ , between the two projected C-N bonds is then a measure of the ring puckering. In MoO₃·dien, θ is 55.9° . In [Co(en)₃]³⁺ it was found to be 48° and Corey and Bailar showed that this is a reasonable value in the light of an elementary conformational analysis. The somewhat larger angle found here is most likely due mainly to the greater metal-nitrogen distance (~ 2.3 vs. ~ 2.0 Å.). The fact that

TABLE IV
INTRAMOLECULAR INTERATOMIC DISTANCES AND STANDARD DEVIATIONS, Å.

Bond distances		Nonbonded distances	
Mo-O ₁	1.739 ± 0.008	O ₁ -O ₂	2.805 ± 0.014
Mo-O ₂	1.735 ± 0.006	O ₂ -O ₂ '	2.776 ± 0.010
Mo-N ₁	2.332 ± 0.009	N ₁ -N ₂	2.770 ± 0.014
Mo-N ₂	2.320 ± 0.006	N ₂ -N ₂ '	2.982 ± 0.011
N ₁ -C ₁	1.457 ± 0.016	O ₁ -N ₂	2.850 ± 0.012
N ₂ -C ₂	1.484 ± 0.015	O ₂ -N ₂	2.797 ± 0.010
C ₁ -C ₂	1.549 ± 0.016	N ₁ -C ₂	2.495 ± 0.016
		N ₂ -C ₁	2.444 ± 0.013
		C ₁ -C ₁	2.454 ± 0.015
		C ₂ -C ₂ '	3.224 ± 0.015

TABLE V
BOND ANGLES AND STANDARD DEVIATIONS, DEGREES

O ₁ -Mo-O ₂	106.8 ± 0.3
O ₂ -Mo-O ₂ '	105.3 ± 0.3
N ₁ -Mo-N ₂	73.1 ± 0.4
N ₂ -Mo-N ₂ '	80.0 ± 0.3
O ₁ -Mo-N ₂	88.0 ± 0.4
O ₂ -Mo-N ₂	86.0 ± 0.4
O ₂ -Mo-N ₁	88.2 ± 0.4
N ₁ -C ₁ -C ₂	111.2 ± 0.8
N ₂ -C ₂ -C ₁	106.3 ± 0.8
C ₁ -N ₁ -C ₁ '	113.8 ± 1.0

the two chelate rings are not independent, but fused on a common Mo-N bond, may also influence the puckering.

The C-N and C-C distances and the N-C-C and C-N-C angles all appear reasonable and of no special interest.

Hydrogen Bonding.—This is illustrated in Fig. 2. Each amine hydrogen atom participates in a hydrogen bond to an oxygen atom of a neighboring molecule. Each of the O₂ type oxygen atoms in each molecule participates in two hydrogen bonds. The N ··· O distances and their standard deviations in the three crystallographically distinct hydrogen bonds are: N₁ ··· O₁, 2.875 ± 0.021 Å.; N₂ ··· O₂, 2.943 ± 0.015 Å.; N₂ ··· O₂', 3.043 ± 0.015 Å. The hydrogen atoms appear to lie slightly off the N ··· O lines, but these displacements are within the considerable uncertainties in their coordinates. We have no truly objective assessment of these uncertainties, but feel from the features of the difference Fourier functions used to obtain the coordinates that standard deviations of ~ 0.1 Å. may be reasonable.

The hydrogen bonds form a continuous net throughout the crystal and doubtless play an important role in the packing of the molecules. None of them, however, appears to be of more than average strength,¹⁰ and that from N₂ ··· O₂' is, in fact, relatively weak.

Acknowledgment.—We thank Dr. J. S. Wood and Mr. W. A. Dollase for helpful advice, and the M.I.T. Computation Center for access to the IBM 7090 computer.

(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

(6) F. A. Kruse, *Acta Cryst.*, **14**, 1035 (1961).

(7) E. Amble, *et al.*, *J. Chem. Phys.*, **20**, 192 (1952).

(8) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(9) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 158 (1957).