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Synthesis and Crystal Chemistry of $NH_3(MoO_3)_3$

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$NH_3(MoO_3)_3$ crystallizes with hexagonal symmetry, space group $P6_3/m$, lattice constants $a = 10.568$ Å, $c = 3.726$ Å, and $Z = 2$. The crystal structure has been determined by Patterson synthesis and refined assuming isotropic temperature factors to a final conventional R value of 0.085. The structure shows a three-dimensional arrangement built up of double chains of distorted MoO_6 octahedra, parallel to the [001] direction. The octahedral double chains are linked among each other through common oxygen atoms. In addition to the shared oxygen atoms, each molybdenum is coordinated to one terminal oxygen. Mo–O distances range from 1.645 to 2.378 Å and O–Mo–O angles from 74.3 to 114.3°. These results are consistent with the fact that molybdenum in high-valence states shows octahedral coordination with terminal oxygens.

Introduction

Molybdenum compounds have been given considerable attention because of the interest in the chemistry of the transition metals and their industrial applications. Ammonium molybdates constitute important kinds of compounds for applications demanding high-purity molybdenum trioxide. Production of ammonium molybdates is usually used as a purification step in obtaining pure raw material for metal powder and steelmaking purposes.

It is well known that many compounds are formed in the ternary system NH_3–MoO_3–H_2O but few crystal chemistry data have been reported (*1–8*). This paper reports the crystallography and structure determination of $NH_3(MoO_3)_3$.

Experimental

Powder and single crystals of $NH_3(MoO_3)_3$ were prepared by direct reaction of MoO_3, NH_3, and H_2O in sealed glass vessels. Reagent-grade MoO_3 and NH_3 (E. Merck) were mixed with distilled water in a molar weight ratio of $11MoO_3 : 8NH_3 : 81H_2O$, and then heated at 80°C for a period of 20 days. Chemical equilibrium was monitored by measuring the partial pressure of NH_3. Quantitative reaction is achieved when the pressure reaches a constant value. Colorless and transparent prismatic single crystals of about 0.05-mm length, free from inclusions and twins, were obtained on the bottom of the vessel. The specimens were chemically identified by usual analysis techniques. The content of NH_3(3.70 wt%) was determined by the Kjedahl method and molybdenum trioxide (96.3 wt%) by the Jones reduction technique.

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The unit formula of the sample, as calculated from these data, was found to be $NH_3(MoO_3)_3$. Magnetic measurements conducted on the substance showed diamagnetic behavior, which means that molybdenum exhibits a hexavalent state in the compound. This allowed us to conclude that it is not a true ammonium molybdate, which was later corroborated by the fact that the N atoms are located in $\bar{3}$ symmetry site, and that an ammonium group cannot fit into such a site.

The infrared spectrum of the substance (recorded in a Nujol mull) showed a peak at 1400 cm^{-1} in the range of the N–H stretching frequencies.

By thermoanalytical measurements it was found that decomposition into MoO_3 and NH_3 under atmospheric pressure takes place at 400°C. The resulting solid phase was unambiguously identified as MoO_3, and the weight loss was 3.72 wt%, corresponding to the NH_3 content.

The crystallinity of the specimens was checked by optical and scanning microscopy. The single crystals, selected under the microscope, showed well-defined faces with habit form {100} (with respect to the unit cell) making up a parallellohedral prism with edges parallel to the c axis. The angle between (100) and (010) planes measured 120° and the faces (100) and ($\bar{1}00$) were parallel.

Crystallographic Data

A single crystal ([110] direction parallel to the axis of the goniometer head) was examined by rotation, Weissenberg, precession, and cone-axis photographs (Ni-filter CuK_α radiation). Diffraction patterns taken with MoK_α radiation disclosed very faint reflections, even with long exposure times. Laue symmetry and systematic extinctions ($00l : l = 2n$) showed $P6_3$ and $P6_3/m$ as the possible space groups. Owing to the presence of a symmetry plane normal to the c axis, detected from oscillation diagrams, $P6_3/m$ (C^2_{6h}) was considered the correct space group. The powder data were collected with a Debye–Scherrer camera and a standard diffractometer (Hilger and Watts Y144, internal calibration with Si powder (*9*, *10*) CuK_α radiation). The lattice parameters refined from these data by a standard least-squares program (*11*) are given in Table I and the powder data in Table II. The density was measured with a capillarity pycnometer.

Crystal Structure Determination and Refinement

From a single crystal a total of 234 independent reflections were measured (Enraf–Nonius Cad-4 Four Circle Automatic Diffractometer, graphite-monochromated MoK_α radiation, [110] direction parallel to the ϕ axis). Intensities were collected up to $\sin\theta/\lambda = 0.548$ Å^{-1}. A total of 165 reflections were selected for the calculation according to the criterion $I \geq 3\sigma(I)$, $\sigma(I)$ being the estimated standard deviation based on counting statistics. The data were corrected for background and Lorentz-polarization effects. In spite of the very small size of the crystal, correction for spherical absorption was performed.

TABLE I

CRYSTALLOGRAPHIC DATA FOR $NH_3(MoO_3)_3$

Space group	$P6_3/m$
a	10.568 Å
c	3.726 Å
V	360.4 Å^3
FW	448.8
D_{293}	4.100 mg m^{-3}
D_x	4.137 mg m^{-3}
Z	2
$\mu(MoK_\alpha)$	50.2 cm^{-1}
Crystal size	
Length	0.05 mm
Diameter	0.04 mm

TABLE II

X-RAY POWDER DIFFRACTION PATTERN OF $NH_3(MoO_3)_3$

d_{obs}(Å)	d_{cal}(Å)	*h k l*	I/I_0	d_{obs}(Å)	d_{cal}(Å)	*h k l*	I/I_0
9.200	9.152	1 0 0	41	1.412	1.412	6 0 1	<1
5.312	5.284	1 1 0	3	1.394	1.396	6 1 0	1
4.583	4.576	2 0 0	15		1.395	4 3 1	
3.453	3.459	2 1 0	100		1.394	3 2 2	
	3.451	1 0 1		1.363	1.364	5 2 1	1
3.053	3.048	1 1 1	5		1.362	4 1 2	
2.894	2.889	2 0 1	<1	1.307	1.308	3 5 0, 7 0 0	<1
2.644	2.642	2 2 0	2		1.307	6 1 1	
2.542	2.538	3 1 0	6		1.306	5 0 2	
	2.535	2 1 1		1.280	1.280	3 3 2	<1
2.156	2.155	2 2 1	<1	1.267	1.269	6 2 0	<1
2.100	2.100	3 2 0	4		1.268	4 2 2	
1.999	1.997	4 1 0	8	1.233	1.234	5 3 4, 7 0 1	<1
1.951	1.950	4 0 1	1		1.233	5 1 2	
1.867	1.863	0 0 2	1		1.231	1 0 3	
1.829	1.830	5 0 0	2	1.211	1.212	7 1 0	<1
	1.829	3 2 1			1.209	1 1 2	
	1.826	1 0 2		1.201	1.201	6 2 1	<1
1.760	1.761	3 3 0	<1		1.199	2 0 3	
	1.757	1 1 2		1.170	1.172	5 4 0	<1
1.728	1.730	4 2 0	<1		1.171	3 4 2	
	1.726	2 0 2			1.169	2 1 3	
1.642	1.643	5 0 1	3	1.152	1.153	6 3 0, 7 1 1	<1
	1.640	2 1 2			1.152	5 2 2	
1.592	1.592	3 3 1	1		1.150	3 0 3	
1.568	1.569	4 2 1	1	1.118	1.118	7 2 0, 5 4 1	<1
1.523	1.525	6 0 0	<1		1.117	6 1 2	
	1.523	2 2 2			1.116	3 1 3	
1.465	1.465	5 2 0	<1	1.093	1.094	8 0 1	<1
1.445	1.445	4 0 2	<1		1.092	4 0 3	

Approximate positions of Mo atoms were deduced from three-dimensional Patterson maps. The resulting Mo–Mo distances of about 3.30, 3.73, and 4.03 Å agreed reasonably with the values corresponding to MoO_6 octahedra connected by sharing edges or corners in related compounds such as MoO_3 (*12, 13*). After location of Mo atoms an ideal model including O and N atoms was derived from stereochemical considerations and then refined by the full-matrix least-squares technique, assuming isotropic temperature factors for all atoms in the structure. The minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, yielded a conventional *R* value of 0.085. Since different weighting schemes yielded about the same results, all reflections were given unit weight. The atomic scattering factors for all nonhydrogen atoms and correction for anomalous scattering were taken from International Tables for X-Ray Crystallography (*14*). Table III lists the final positional and isotropic parameters with their estimated standard deviations.

Description and Discussion of the Structure

Each molybdenum atom in $NH_3(MoO_3)_3$

TABLE III

ATOMIC POSITIONAL COORDINATES AND THERMAL PARAMETERS IN $NH_3(MoO_3)$[a]

Atom	x	y	z	B (Å^2)
Mo	0.6445(4)	0.5418(4)	0.25	0.97(8)
O(1)	0.771 (3)	0.489 (3)	0.25	1.2 (1)
O(2)	0.713 (3)	0.720 (3)	0.25	0.7 (1)
O(3)	0.415 (3)	0.492 (3)	0.25	0.7 (1)
N	0.0	0.0	0.0	11.5 (5)

[a] Standard deviations in the last digit are given in parentheses.

is octahedrally coordinated by six oxygen atoms. The structure shows a three-dimensional arrangement built up of double chains of distorted MoO_6 octahedra, parallel to the [001] direction. Each octahedron shares two edges with neighboring ones, which causes characteristic zig-zag stacking along the [001] direction, as shown in Fig. 1a. The octahedral double chains are linked among each other through common oxygen atoms, as indicated in Fig. 2. In addition to the bridge-forming oxygen atoms, each molybdenum atom is coordinated to one terminal oxygen.

Table IV contains the interatomic distances and angles. The MoO_6 octahedra are strongly distorted. There are two very short Mo–O lengths of 1.645 and 1.686 Å to the terminal oxygen O(2) and the edge-bridging oxygen O(1), two medium Mo–O distances of 1.941 Å to O(5) and O(6) and finally two very long Mo–O bonds of 2.209 and 2.378 Å to the corner-sharing oxygens O(3) and O(4). The average of the Mo–O bond

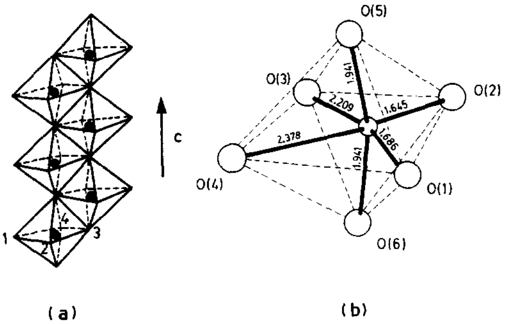

FIG. 1. Stacking of MoO_6 octahedra along the c axis, and interatomic distances (Å) in the oxygen coordination octahedron.

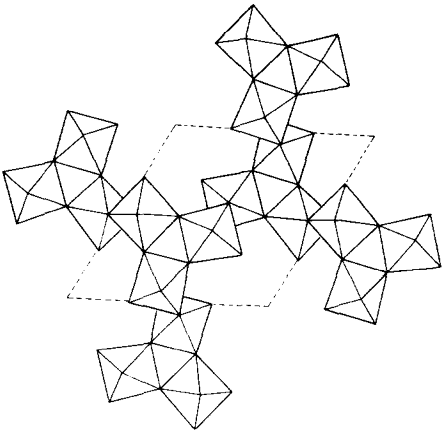

FIG. 2. MoO_6 octahedra projected down the c axis.

TABLE IV

INTERATOMIC DISTANCES AND BOND ANGLES IN THE STRUCTURE OF $NH_3(MoO_3)_3$[a]

(a) MoO_6 octahedron			
Mo–O(1)	1.686(5) Å	O(1)–O(5)	2.787(6) Å
Mo–O(2)	1.645(5)	O(2)–O(3)	2.852(6)
Mo–O(3)	2.209(5)	O(2)–O(5)	2.699(6)
Mo–O(4)	2.378(5)	O(3)–O(4)	2.864(6)
Mo–O(5)	1.941(5)	O(3)–O(5)	2.534(6)
O(1)–O(2)	2.798(6)	O(4)–O(5)	2.814(6)
O(1)–O(4)	2.514(6)		
O(1)–Mo–O(2)	114.3°	O(2)–Mo–O(4)	97.3°
O(1)–Mo–O(3)	151.5	O(3)–Mo–O(4)	77.2
O(1)–Mo–O(4)	74.3	O(3)–Mo–O(5)	74.9
O(1)–Mo–O(5)	100.2	O(4)–Mo–O(5)	80.6
O(2)–Mo–O(3)	94.3	O(5)–Mo–O(6)	147.3
O(2)–Mo–O(4)	188.5		
(b) Mo–Mo distances			
Mo–Mo	3.298(3) Å	Edge-sharing octahedra	
Mo–Mo	3.726(3)		
Mo–Mo	4.034(3)	Corner-sharing octahedra	
(c) Shortest N–O distance 3.138(6) Å			

[a] Standard deviations in last digit are given in parentheses.

lengths of 1.967 Å may be compared to the corresponding value of 1.981 Å for the MoO_6 octahedra in MoO_3 (*13*).

The kind of octahedral distortion with two very short *cis* Mo–O bonds, two very long bonds in the same plane, and two medium distances to the remaining oxygen atoms, is commonly observed in molybdenum oxygen compounds (*15, 16*). Still shorter distances than Mo–O(2) were reported for others with terminal oxygen atoms (*17*). It has been pointed out that the bond length to a single terminal oxygen is largely independent on the coordination number of Mo(15).

The NH_3 groups lie in the voids formed by six terminal oxygen atoms, located at (0,0,0) and $(0,0,\frac{1}{2})$. Although the positions of hydrogen atoms were not able to be determined, this suggests hydrogen bonding with resonance between those six oxygens, the H being located on mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ in the cell.

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References

1. B. Krebs, *Acta Crystallogr. B* **28,** 2222 (1972).
2. I. Böschen and B. Krebs, *Acta Crystallogr. B* **30,** 1795 (1974).
3. I. Böschen, B. Buss, and B. Krebs, *Acta Crystallogr. B* **30,** 48 (1974).
4. J. Fuchs, H. Hartl, W. D. Hunnius, and S. Mahjour, *Angew. Chem.* **87,** 634 (1975).
5. H. R. Oswald, J. R. Günter, and E. Dubler, *J. Solid State Chem.* **13,** 330 (1975).
6. H. T. Evans, B. M. Gatehouse, and P. Leverett, *J. Chem. Soc. Dalton,* 505 (1975).
7. A. W. Armour, M. G. B. Drew and, P. C. H. Mitchell, *J. Chem. Soc. Dalton,* 1493 (1975).
8. H. Vivier, J. Bernard, and H. Djomaa, *Rev. Chim. Miner.* **14,** 584 (1977).
9. C. R. Hubbard, H. E. Swanson, and F. A. Mauer, *J. Appl. Crystallogr.* **8,** 45 (1975).
10. C. R. Hubbard, *J. Appl. Crystallogr.* **16,** 285 (1983).
11. J. Gvildys, Argonne National Laboratory Program Library B106 (1965).
12. G. Anderson and A. Magneli, *Acta Chem. Scand.* **4,** 793 (1950).
13. L. Kihlborg, *Ark. Kemi* **21,** 357 (1963).
14. "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
15. F. A. Schröder, *Acta Crystallogr. B* **31,** 2294 (1975).
16. C. J. Bart and V. Ragaini, *Acta Crystallogr. B* **36,** 1351 (1980).
17. L. O. Atovmyan and O. N. Krasochka, *Zh. Strukt. Khim.* **13,** 319 (1972).