

BRIEF COMMUNICATIONS

Preparation and Structure of Hexagonal Molybdenum Trioxide

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The phase widely known as "hexagonal MoO₃" is shown to correspond to the partially dehydrated and de-ammoniated ammonium decamolybdate. The latter material has the ideal stoichiometry NH₄Mo₅O₁₅OH·2H₂O. Relationships between a variety of materials with the decamolybdate structure are discussed. A novel preparative route to ammonium decamolybdate is described. © 1987 Academic Press, Inc.

The purpose of this note is to dispel some of the confusion which has arisen in the literature concerning the identity of solid phases variously described as hexagonal molybdenum trioxide hydrate (1), hexagonal molybdenum trioxide (1, 2), molybdic-C-phases (3), and -14 and -22 molybdates (4). The common features which all such phases possess are:

- (a) They contain other metallic elements (or ammonium) in addition to molybdenum;
- (b) molybdenum is present exclusively as Mo(VI);
- (c) their X-ray diffraction patterns can be indexed on the basis of a common hexagonal cell of dimensions $a \sim 10.5 \text{ \AA}$, $c \sim 3.7 \text{ \AA}$ (with $001:1 = 2n$ compatible with space groups $P6_3$ or $P6_{3/m}$);
- (d) their densities fall in the range 3.5 to 4.0 g · cm⁻³ and imply that the elementary cell defined above ($V \sim 360 \text{ \AA}^3$) contains 5-6 atoms of Mo.

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Empirical formulas of the solids concerned are of two types. First, materials prepared by acidification of solutions of alkali metal or ammonium molybdates are formulated as $(A_2O)_x \cdot MoO_3 \cdot (H_2O)_y$ ($0.05 \leq x \leq 0.1$, $y \leq 0.5$), where A = alkali metal or ammonium. The exact values of x and y depend on the details of their preparation and subsequent treatment, particularly the temperature of drying. Measured densities fall in the range 3.5-3.75 g · cm⁻³, implying the presence of ~5 Mo atoms per unit cell. Ammonium-containing compounds referred to as "-14" and "-22" molybdates which were made by Kiss *et al.* (4) by decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ are also of this type (with $x \sim 0.07$ and ~ 0.05 , respectively). Second, compounds having formulas $A_xV_xMo_{1-x}O_3$ (where A = alkali metal or ammonium, and $0.11 < x < 0.14$) have been prepared by thermal decomposition of mixtures of alkali metal (or ammonium) molybdates and vanadates at $>300^\circ\text{C}$ (2, 5). These phases are characterized by

higher densities of $\sim 4 \text{ g} \cdot \text{cm}^{-3}$ which are compatible with 6 (V, Mo) atoms per unit cell.

Complete structure determinations have been made for representative members of the two categories and this information provides a means of rationalizing most of the known facts about a family of compounds which has been studied independently by many workers over the last twenty years.

The structure of $\text{K}_{0.13}\text{V}_{0.13}\text{Mo}_{0.87}\text{O}_3$ was determined by Darriet and Galy (5) and is shown schematically in Fig. 1. It consists of parallel chains of edge sharing $(\text{Mo}/\text{V})\text{O}_6$ octahedra assembled in groups of three via vertex sharing. Large approximately hexagonal tunnels are formed (radius of inscribed sphere $\sim 1.5\text{--}1.6 \text{ \AA}$) which contain potassium ions. The same crystal structure ($P6_3$ or $P6_{3/m}$) was determined by Olenkova *et al.* (2) for the ammonium analog $(\text{NH}_4)_x\text{V}_x\text{Mo}_{1-x}\text{O}_3$. The unit cell contains 6 Mo (or V) atoms on the $6(h)$ sites and $6x \text{ NH}_4^+$ or K^+ ions are distributed over the $2(b)$ sites. Geometrical considerations suggest that only half of these sites may be filled simultaneously, leading to an ideal structural formula of $\text{AVMo}_5\text{O}_{18}$ and a density of $\sim 4.0 \text{ g} \cdot \text{cm}^{-3}$. A hypothetical hexagonal MoO_3 , Mo_6O_{18} , can be derived from this structure

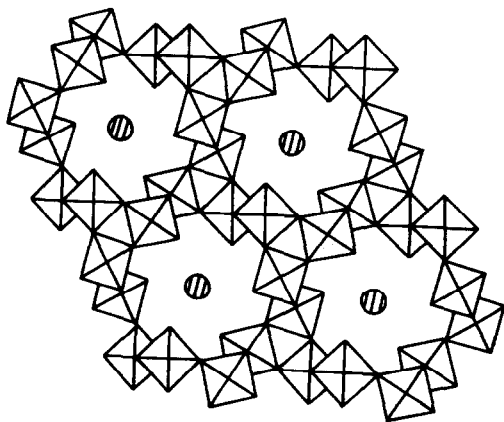


FIG. 1. The structure of $\text{K}_x\text{V}_x\text{Mo}_{1-x}\text{O}_3$ (after Darriet and Galy (5)).

by complete occupation of the $6(h)$ sites by molybdenum and vacant $2(b)$ tunnel sites; however, this compound has not been made so far and some tunnel occupancy by a large cation seems to be necessary to stabilize the structure.

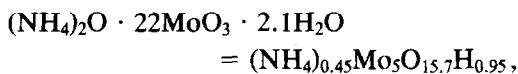
The parent structure for the other class of compound $(\text{A}_2\text{O})_x\text{MoO}_3(\text{H}_2\text{O})_y$ was determined by Krebs and Paulat-Böschen (6) for the so-called potassium decamolybdate $(\text{K}_2\text{O}) \cdot 10\text{MoO}_3 \cdot 5\text{H}_2\text{O}$ (i.e., $\text{KM}_5\text{O}_{18}\text{H}_5$). It has exactly the same K, Mo, O framework as found for $\text{KVM}_5\text{O}_{18}$ but in this case the Mo atoms occupy (randomly) only five-sixths of the $6(h)$ sites (in $P6_{3/m}$) and potassium occupy half the $2(b)$ sites in the large hexagonal tunnels of Fig. 1. The lattice parameters $a = 10.55 \text{ \AA}$, $c = 3.727 \text{ \AA}$ are close to those for $\text{K}_x\text{V}_x\text{Mo}_{1-x}\text{O}_3$ but now the theoretical (and experimental) density is only $3.75 \text{ g} \cdot \text{cm}^{-3}$, significantly lower than would be found if all $6(h)$ sites were occupied by molybdenum ($> 4 \text{ g} \cdot \text{cm}^{-3}$). The absence of a molybdenum atom from the unit cell is of course exactly balanced by the presence of K and H_5 in the structure. That is, the structural formula may be written as $\text{K}_i\text{Mo}_5\text{O}_{18}(\text{H}_5)_i$, where i refers to the interstitial $2(b)$ site and i' to some other interstitial site in the structure. Krebs and Paulat-Böschen suggest that the 5 H's are attached to oxygens surrounding the vacant Mo site by two $-\text{OH}_2$ and one $-\text{OH}$ groups, leading to the formulation of the decamolybdate as $\text{KM}_5\text{O}_{15}(\text{OH}) \cdot 2\text{H}_2\text{O}$.

Acidification of ammonium molybdate solution at $40 < T < 100^\circ\text{C}$ (which are the preparative conditions followed by many of the workers mentioned in the Introduction) leads invariably to a solid phase with ammonia (and sometimes H_2O) contents less than that for the corresponding ideal ammonium decamolybdate $\text{NH}_4\text{Mo}_5\text{O}_{18}\text{H}_5$ (density = $3.64 \text{ g} \cdot \text{cm}^{-3}$), which we believe is the model structure for all the so-called hexagonal- MoO_3 phases. However, we have prepared a compound of this composi-

tion (or very close to it) as follows: about 5 g of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ was stirred overnight at room temperature with $\sim 100 \text{ cm}^3$ of 4 M NH_4Cl solution. A greenish-white solid was filtered off, washed with ice-cold distilled water, and dried at 40°C . Powder X-ray diffraction and infrared data for this material were identical with those recorded for the "ammonium Mo-C" phase by von Peters *et al.* (3) and "hexagonal MoO_3 hydrate" by Sotani (1): X-ray data indexed on the hexagonal cell used by Krebs and Paulat-Böschen are given in Table I for these phases. For products which have lost water (mostly below 200°C) and NH_3 (mostly above 300°C) a reasonable structural formula which accommodates a degree of non-stoichiometry in both NH_3 and H_2O content is



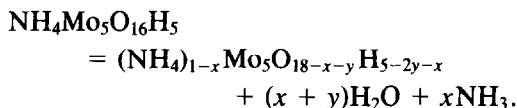
This implies that ammonium ions partially occupy the possible tunnel site and that some O (and H) atoms are lost from the elementary cell. For example: the "14-molybdate" obtained by Kiss *et al.* (4) by the thermal decomposition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was formulated as $(\text{NH}_4)_2\text{O} \cdot 14\text{MoO}_3 \cdot 3.3\text{H}_2\text{O} = (\text{NH}_4)_{0.71}\text{Mo}_5\text{O}_{16.5}\text{H}_{2.3}$. The theoretical density of $3.5 \text{ g} \cdot \text{cm}^{-3}$ for this suggested structural formula compares favorably with their measured value of $3.57 \text{ g} \cdot \text{cm}^{-3}$. The X-ray data of Kiss *et al.* (4) have been reindexed for the hexagonal cell described above and the results given in Table I confirm that this provides a satisfactory scheme. The product obtained by us on heating "ammonium decamolybdate" to 300°C was very close in composition to the "22-molybdate" reported by Kiss *et al.* (4),



and both are indexable on the same hexagonal cell ($a = 10.52 \text{ \AA}$, $c = 3.725 \text{ \AA}$). This compound corresponds in all important respects to that described by Sotani (1) as

"anhydrous $h\text{-MoO}_3$ ". On complete de-ammoniation at $>400^\circ\text{C}$ the hexagonal structure finally collapses and orthorhombic MoO_3 results (1).

A notable feature of the partially de-ammoniated and dehydrated ammonium decamolybdate (i.e., "anhydrous $h\text{-MoO}_3$ ") is its capacity to reabsorb both ammonia and water vapor (7, 8):



This is a natural consequence of the retention of the tunneled ammonium decamolybdate structure and temperatures up to $\sim 350^\circ\text{C}$. Reabsorption of both H_2O vapor and NH_3 gas onto "anhydrous $h\text{-MoO}_3$ " at lower temperatures has been studied by Sotani *et al.* (7). The quantities reported for water and strongly bound ammonia conform to the limits imposed by this equation. Moreover, X-ray and infrared data confirm that the characteristic hexagonal lattice is retained throughout and ammonia is reabsorbed principally as NH_4^+ ($\nu_4 \sim 1400 \text{ cm}^{-1}$). The latter implies the presence, in "anhydrous $h\text{-MoO}_3$ " or the "22-molybdate" of Kiss *et al.*, of bulk hydrogens and not merely the presence of "acidic" surface sites.

Recently the structure of a compound formulated as $(\text{NH}_3)(\text{MoO}_3)_3$ has been reported by Garin and Blanc (9). This compound was said to be formed by reaction between MoO_3 , NH_3 , and H_2O in a sealed tube at 353 K. The reported powder X-ray pattern and cell constants are almost identical with those of ammonium decamolybdate (Table I). Although refinement of the crystal structure of " $\text{NH}_3(\text{MoO}_3)_3$ " by Garin and Blanc in $P6_3/m$ placed Mo and O atoms in the same sites described by Krebs and Paulat-Böschen (6) for potassium decamolybdate, 6 Mo atoms rather than 5 were placed in the unit cell and NH_3 molecules rather than NH_4^+ ions were assumed to oc-

TABLE I
POWDER X-RAY DATA

<i>I</i> ^a	<i>k k l</i>	This work ^b		Literature materials			
		<i>d</i> _{calc} (Å)	<i>d</i> _{obs} (Å)	<i>d</i> _{obs} ^c (Å)	<i>d</i> _{obs} ^d (Å)	<i>d</i> _{obs} ^e (Å)	<i>d</i> _{obs} ^f (Å)
s	1 0 0	9.16	9.16	9.33	9.224	9.200	9.1
w	1 1 0	5.29	5.29	5.34	5.301	5.312	5.24
m	2 0 0	4.58	4.58	4.62	4.585	4.583	4.54
vs	2 1 0	3.46	3.46	3.48	3.462	3.453	3.43
	1 0 1	3.45					
s	3 0 0	3.05	3.05	3.06	3.046	3.053	3.02
	1 1 1	3.05					
w	2 0 1	2.891	2.893	2.90	2.889	2.894	2.86
w	2 2 0	2.645	2.646	2.660	2.641	2.644	2.61
s	3 1 0	2.541	2.536	2.551	2.534	2.542	2.51
	2 1 1	2.536					
m	2 2 1	2.157	2.156	2.167	2.153	2.156	2.139
m	3 2 0	2.102	2.103	2.111	2.096	2.100	2.083
	3 1 1	2.100					
w	4 1 0	1.999	2.002	2.008	1.994	1.999	1.981
m	4 0 1	1.951	1.951	1.960	1.947	1.951	1.934
m	0 0 2	1.863	1.860	1.872	1.862	1.867	1.851
m	5 0 0	1.832	1.832	1.837	1.825	1.829	1.814
	3 2 1	1.831					
m	1 0 2	1.826	1.824				
w	3 3 0	1.763	1.765	1.771	1.757	1.760	1.746
	4 1 1	1.762					
m	4 2 0	1.731	1.734	1.735	1.724	1.728	1.713
m	2 0 2	1.726	1.725				
m	5 1 0	1.645	1.646	1.647	1.638	1.642	1.629
	5 0 1	1.644					
m	2 1 2	1.641	1.640				
m	3 3 1	1.594	1.594	1.600	1.588	1.592	1.580
	3 0 2	1.590					

^a Visually estimated intensities: s, strong; m, medium; w, weak; vs, very strong.

^b Refined lattice parameters for ammonium decamolybdate $\text{NH}_4\text{Mo}_5\text{O}_{18}\text{H}_5$ prepared in this work: $a = 10.58(1)$, $c = 3.726(2)$ Å.

^c Observed d spacings as given in Ref. (3) for "ammonium-C-phase." Refined lattice parameters: $a = 10.628(3)$, $c = 3.744(1)$ Å (originally indexed as cubic, $a = 12.98(2)$ Å).

^d Observed d spacings as given in Ref. (4) for "14-molybdate": $(\text{NH}_4)_2\text{O} \cdot \text{Mo}_{14}\text{O}_{42}$. Refined lattice parameters: $a = 10.552(3)$, $c = 3.723(1)$ Å (originally indexed as cubic, $a = 12.90$ Å).

^e Observed d spacings as given in Ref. (9) for $(\text{NH}_3)_{0.33}\text{MoO}_3$. Refined lattice parameters: $a = 10.568$, $c = 3.726$ Å.

^f Observed d spacings as given in Ref. (5) for $\text{K}_{0.13}\text{V}_{0.13}\text{Mo}_{0.87}\text{O}_3$. Refined lattice parameters: $a = 10.481(5)$, $c = 3.701(3)$ Å.

cupy the 2(b) tunnel sites. The presence of neutral ammonia molecules (rather than cations) makes less good chemical sense and the analytical formula requires *both* 2(b) sites to be occupied simultaneously in " $\text{NH}_3(\text{MoO}_3)_3$ " in contrast to the more acceptable occupancy of half these sites in $\text{K}_x\text{V}_x\text{Mo}_{1-x}\text{O}_3$ and $\text{KMo}_5\text{O}_{15}(\text{OH})\cdot 2\text{H}_2\text{O}$. The infrared band reported by Garin and Blanc at $\sim 1400\text{ cm}^{-1}$ could most reasonably be assigned to the characteristic deformation mode ν_4 of NH_4^+ and not to a N-H stretch ($3000\text{--}3500\text{ cm}^{-1}$ (10)) as they postulate. Since it has been demonstrated that the family of compounds based on the decamolybdate structure is a broad one it seems to us that further careful confirmatory chemical analysis and density measurements are needed before " $\text{NH}_3(\text{MoO}_3)_3$ " can be completely accepted as a new compound rather than a further example of a partially de-ammoniated and dehydrated ammonium decamolybdate phase.

Acknowledgments

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Note added in proof. An identification of polymolybdates of the analytical ratio $\text{A}_2\text{O} \cdot \text{MoO}_3 = 1:10$ to

~ 30 (including the "phase-C" molybdates) with the "decamolybdate" type was reported by K. H. Tytko in a note added in proof (p. 24) to the recent Gmelin Supplement, Volume B4 (1985), and referred to the work of G. Baethe (Diss. Göttingen, West Germany, 1985). This information was not available to us at the time of writing and our conclusions, which support this statement, were arrived at independently.

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