

# Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> and Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> · 2CH<sub>3</sub>OH: New Structural Insights Derived from Reaction Chemistry and Diffraction Techniques

E. M. McCarron III,<sup>1</sup> R. L. Harlow I, Z. G. Li, C. Suto,<sup>2</sup> and Y. Yuen<sup>2</sup>

Central Research and Development, The DuPont Company, Experimental Station, 356/341, Wilmington, Delaware 19880-0356

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The reaction of molybdenum trioxide dihydrate, MoO<sub>3</sub> · 2H<sub>2</sub>O, with methanol produces the title compounds. That these molybdenum oxy-methoxides decompose with liberation of CH<sub>2</sub>O suggests that they represent exquisite models for selective oxidation of methanol to formaldehyde over molybdate catalysts. Although a number of physical techniques have been employed to elucidate certain structural features, the actual structures remain unknown. However, their unit cells have been determined for the first time by employing the complimentary nature of electron and powder diffraction techniques. This information coupled with structural insights derived from careful studies of the reaction chemistry, in particular, the synthesis and characterization of a new amorphous intermediate, MoO<sub>3</sub> · CH<sub>3</sub>OH, has allowed fairly detailed structures for these interesting molybdenum oxy-methoxide materials to be proposed. © 1998

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## INTRODUCTION

Interest in understanding the mechanism of the selective oxidation of methanol to formaldehyde over molybdate catalysts (1) naturally led to attempts to synthesize model compounds, i.e., compounds which would hopefully mimic certain aspects of the heterogeneous catalytic process (2). One such compound was Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> (3) made by the interaction of MoO<sub>3</sub> · 2H<sub>2</sub>O with CH<sub>3</sub>OH. A slight modification of the reaction conditions resulted in the formation of the closely related Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> · 2CH<sub>3</sub>OH (3). Analogous to the catalytic process, these oxy-methoxides were observed to decompose with liberation of CH<sub>2</sub>O. Figure 1 illustrates the 1:1 correspondence between the catalytic cycle and the reaction chemistry observed for this model system.

While the results of numerous physical studies allowed us to propose what at the time appeared to be a reasonable

model for the Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> structure (2), the inability to either grow single crystals or to index the X-ray powder pattern has prohibited confirmation by standard diffraction techniques. In this paper we make use of the complimentary nature of electron and powder diffraction to determine the unit cell parameters of these two molybdenum oxy-methoxides. Moreover, this new structural information, coupled with insights gleaned from detailed studies of reaction chemistry, has allowed us to propose a new structure for these materials which is in agreement with all the physical data collected to date with the peculiar exception of the X-ray structure factors themselves.

## EXPERIMENTAL

Reaction chemistry was carried out as previously described (3). Comparative thermogravimetric analyses (TGA) were performed on a Cahn TG-171 instrument in flowing O<sub>2</sub> at a heating rate of 10°C/min. A JEM-200EX (at 200 kV accelerated voltage) microscope, equipped with Gatan 1024 × 1024 CCD camera, was used to obtain electron diffraction patterns on these samples which were directly deposited on conventional transmission electron micrograph (TEM) grids. High-resolution, X-ray powder diffraction patterns were obtained at the National Synchrotron Light Source which is a DOE user facility located at Brookhaven National Laboratory, Upton, New York. The samples were mounted in capillaries and the patterns collected at beamlines X3b1 and X7a. In either case, an Si(111) monochromator, a Ge(200) analyzer, and slits on the order of 1 × 8 mm were used in conjunction with a scintillation counter to achieve the highest possible resolution and signal-to-noise ratio.

## RESULTS

### Reaction Chemistry

In earlier papers (2, 3), it was reported that the reaction of yellow crystalline MoO<sub>3</sub> · 2H<sub>2</sub>O with neat CH<sub>3</sub>OH produced two white crystalline compounds, Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> and

<sup>1</sup> E-mail: e.m.mccarron@usa.dupont.com.

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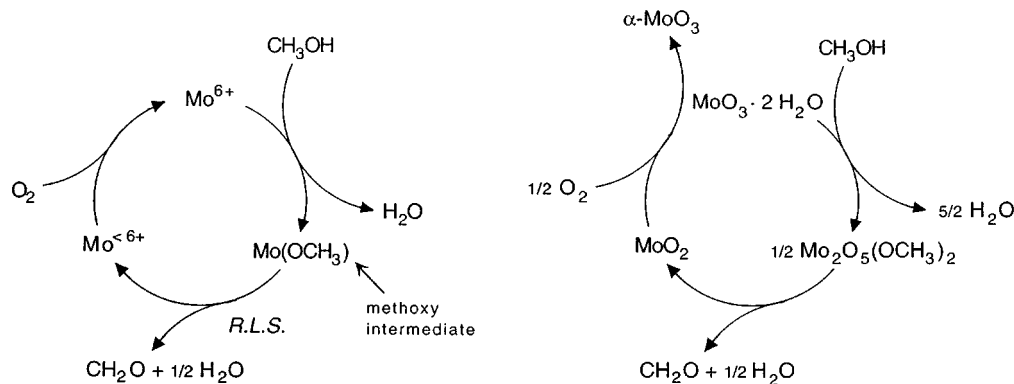
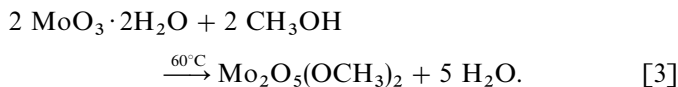
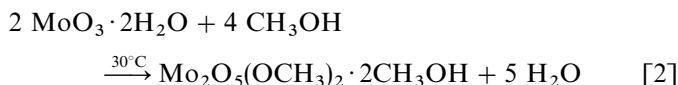
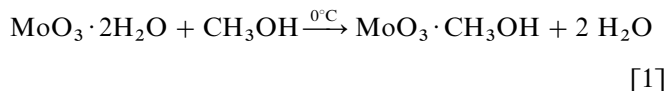


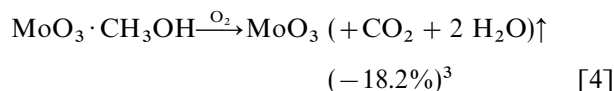
FIG. 1. Diagrams of the heterogeneous catalytic cycle (left) and the model system (right).

Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH. In the present study, not only these two compounds, but also a third compound, white amorphous MoO<sub>3</sub>·CH<sub>3</sub>OH, was found. Compound formation is controlled by the reaction temperature

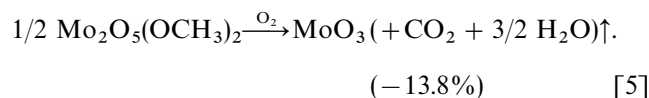


Furthermore, the reaction of the hydrate with methanol to yield the methoxides was found not to be limited to just the yellow monohydrate and dihydrate, but to occur with both the white monohydrate MoO<sub>3</sub>·H<sub>2</sub>O and white hemihydrate MoO<sub>3</sub>·1/2H<sub>2</sub>O as well.

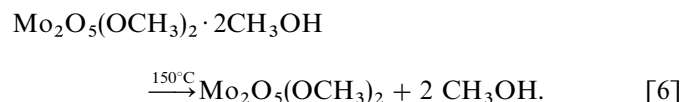
Besides the compositional difference implied by the fact that MoO<sub>3</sub>·CH<sub>3</sub>OH converts to Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> through the intermediate Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH, these closely related compounds are clearly distinguished by their TGA traces (shown in Fig. 2). The TGA of the methanolate and methoxide are representative of the following decomposition reactions:



<sup>3</sup> That the loss of methanol occurs at temperatures only slightly above ambient is reflected in the observed loss being slightly less than theoretical (~2%) (see Fig. 2).



The product of the decomposition reactions is α-MoO<sub>3</sub> as determined by X-ray powder diffraction. Finally, conversion of the intermediate Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH to the methoxide can be accomplished simply by gentle heating (3)



#### Diffraction Data—Unit Cells

Partial cell information, obtained from selected area electron diffraction (SAED) patterns, was used to guide the indexing and to confirm the results. Figure 3 shows both a TEM of and an SAED pattern for Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>. Lattice parameters for crystalline Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH and Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> were determined from peak positions in their synchrotron diffraction patterns using the indexing program TREOR. They are listed in Table 1. Table 2 lists the powder patterns for these materials.

#### Diffraction Data—Structure Refinement

The synchrotron diffraction patterns of Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH and Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> are generally characterized by anisotropically broadened peaks which not only hindered the unit cell determinations, but also suggested that structure determinations would not be possible. This has proven true for Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>·2CH<sub>3</sub>OH. In the case of Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub>, however, a Patterson map based on intensities obtained from a LeBail extraction, contained peaks which could easily be interpreted as one Mo atom situated

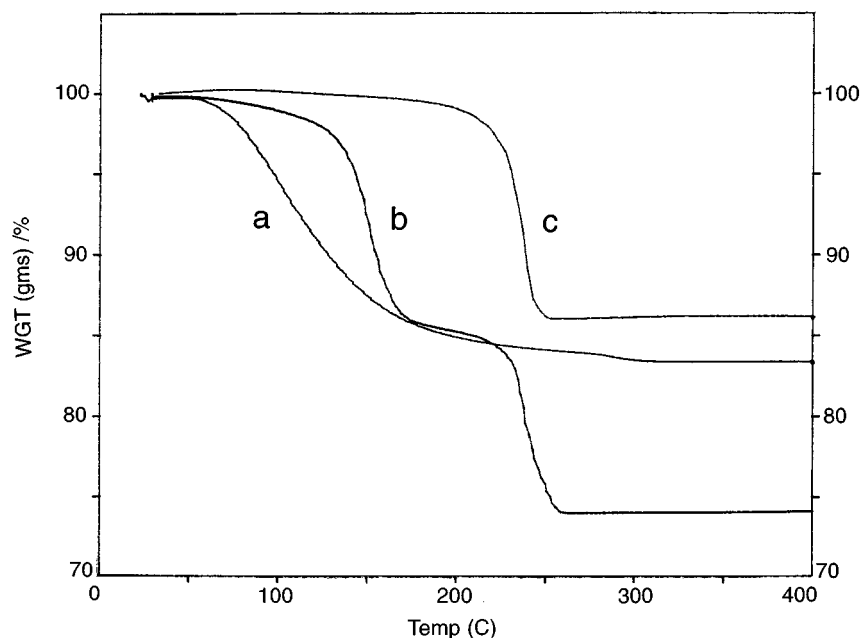


FIG. 2. Thermogravimetric analysis (in air;  $10^\circ\text{C}/\text{min}$ ) of (a)  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$ , (b)  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2 \cdot 2\text{CH}_3\text{OH}$ , and (c)  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$ .

on a mirror plane in space group  $P2_1/m$ . Subsequent Fourier maps suggested that the Mo was five coordinate with three oxygen atoms in the mirror plane and two, one above and one below the plane, in the direction of the  $c$ -axis. The packing which results from this model shows that the structure consists of sheets of  $\text{MoO}(a)_{2/2}\text{O}(e)_{2/2}\text{O}(e)_{1/1}$  trigonal bipyramids (apically shared along the  $c$ -axis and equatorially along  $b$  with one equatorial oxygen unique) which

stack along the  $a$ -axis. Attempts to locate the methyl group have not been successful although there is sufficient space between the sheets to accommodate this moiety. The fit between the observed and calculated intensities based on this model is quite good: The present Bragg  $R$  value is approximately 0.08. However, it has not been possible to reconcile this Mo coordination with the chemical formula  $\text{MoO}_{2.5}(\text{OCH}_3)$ .

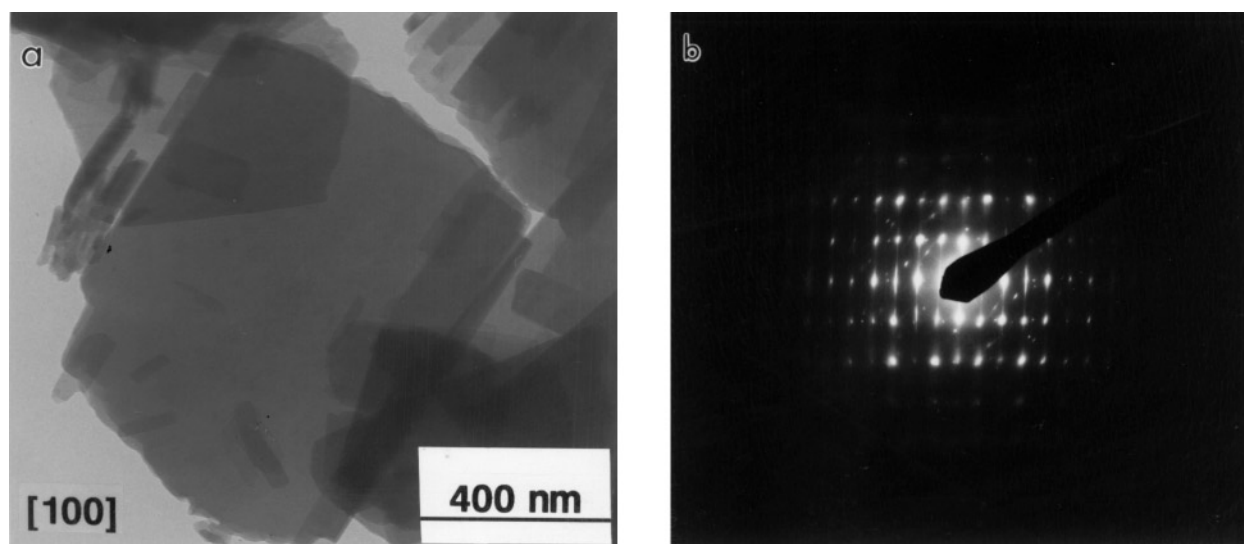


FIG. 3. (a) TEM photograph of  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  showing the plate-like crystal habit and (b) SAED photograph taken normal to the plane of the plate (parallel to  $[100]$ ).

**TABLE 1**  
**Unit Cell Data**

System	Mo <sub>2</sub> O <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub> · 2CH <sub>3</sub> OH	Mo <sub>2</sub> O <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub>
	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/m</i> or <i>P2<sub>1</sub></i>
<i>a</i>	8.0535 (6)	7.600 (2) Å
<i>b</i>	11.6648 (11)	6.208 (2) Å
<i>c</i>	6.2910 (4)	3.953 (1) Å
$\beta$	98.918 (6)	102.55 (1) <sup>o</sup>
<i>V</i>	583.85	182.0 Å <sup>3</sup>
Interlayer spacing	11.6648 (11)	7.418 (2) Å

### DISCUSSION

Table 3 lists physical observations made in previous studies on the methoxides along with structural inferences taken from them. Based primarily upon these inferences and in the absence of any unit cell data, a structure for Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> was proposed (2) which is almost certainly wrong. The structure consisted of stacked double layers of MoO<sub>5/2</sub>(OCH<sub>3</sub>)<sub>1/1</sub> corner-sharing octahedra (ReO<sub>3</sub> type). While this structure fits the requirements of low dimensionality and a single carbon environment, it does not pass a simple color test. Mo(VI) oxide and oxides containing covalently bound adducts, which are based on an ReO<sub>3</sub>-type corner sharing through oxygen, appear intensely yellow colored (e.g.,  $\beta$ -MoO<sub>3</sub> (4), MoO<sub>3</sub> · 2H<sub>2</sub>O (5), and MoO<sub>3</sub> · C<sub>5</sub>H<sub>5</sub>N (6)). A white coloration, on the other hand, is indicative of the edge-sharing double chain motif (as shown in Fig. 4b) found in  $\alpha$ -MoO<sub>3</sub> itself (7), MoO<sub>3</sub> · H<sub>2</sub>O (8,9), and MoO<sub>3</sub> · 1/2H<sub>2</sub>O (10). Note particularly that in the case of the hydrolysis of white Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> the product is the white hemihydrate (3) further supporting this conjecture. Thus, any new structure proposed for Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> ought to include this edge-sharing double chain structural element.

As seen in Fig. 3, Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> has a plate-like morphology. Electron diffraction patterns taken normal to the plate dimension confirm that the plane of the plate contains the *b*- and *c*-axes. Based upon the moderate heating conditions necessary for conversion of Mo<sub>2</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>2</sub> · 2CH<sub>3</sub>OH to methoxide (Eq. 6), it appears reasonable to conclude that it ought to be made up of the same basic structural units as the end-product itself. Thus, one might expect to find some correlation between the lattice parameters of these two materials. The unit cell data are listed in Table 1. Indeed, one finds that

$$b_{\text{methoxide}} \approx c_{\text{intermediate}}$$

$$c_{\text{methoxide}} \approx 1/2 a_{\text{intermediate}}$$

leaving  $a_{\text{methoxide}}$  and  $b_{\text{intermediate}}$  as the unique axes.

**TABLE 2**  
**Powder Patterns**

<i>h</i>	<i>k</i>	<i>l</i>	Mo <sub>2</sub> O <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub> · 2CH <sub>3</sub> OH		Intensity
			<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	
0	1	0	11.6648		
1	0	0	7.9561	7.88	100
1	1	0	6.5728		
0	2	0	5.8324	5.78	48
0	1	1	5.4850		
1	1	-1	4.8356	4.82	20
1	2	0	4.7039	4.69	37
0	2	1	4.2529	4.23	28
1	1	1	4.2522		
1	2	-1	3.9279	3.93	17
0	3	0	3.8883	3.75	2
2	1	0	3.7651	3.75	2
1	2	1	3.5955	3.58	31
1	3	0	3.4934	3.48	21
2	1	-1	3.4526		
0	3	1	3.2963	3.41	7
2	2	0	3.2864	3.28	7
1	3	-1	3.1379		
0	0	2	3.1075	3.09	24
2	2	-1	3.0724	3.06	56

<i>h</i>	<i>k</i>	<i>l</i>	Mo <sub>2</sub> O <sub>5</sub> (OCH <sub>3</sub> ) <sub>2</sub>		Intensity
			<i>d</i> <sub>calc</sub>	<i>d</i> <sub>obs</sub>	
1	0	0	7.4184	7.4186	100
0	1	0	6.2080		
1	1	0	4.7609	4.7610	60
0	0	1	3.8585	3.8584	40
1	0	-1	3.7755	3.7750	25
2	0	0	3.7092	3.7093	2
0	1	1	3.2771	3.2770	5
1	1	-1	3.2258	3.2255	40
2	1	0	3.1841	3.1842	15
1	0	1	3.1541	3.1542	5
0	2	0	3.1040	3.1040	40
2	0	-1	3.0222	3.0218	1
1	2	0	2.8634	2.8635	20

*Note.* The patterns are only listed to  $d \sim 3.0$  as the diffraction peaks broaden and their intensity falls off rapidly.

Furthermore, as a check of the validity of the unit cells and also the underlying assumption that the structural units are in fact the same, one might expect the following relationship to hold true<sup>4</sup>:

$$2(V_{\text{methoxide}} + 2V_{\text{methanol}}^5) \approx V_{\text{intermediate}}$$

$$2(182.0 + 2(52.4))\text{\AA}^3 \approx V_{\text{intermediate}}$$

$$573.6 \text{\AA}^3 \approx 584.9 \text{\AA}^3.$$

<sup>4</sup>The factor 2 is associated with the doubling of *a*-axis of the intermediate relative to the *c*-axis of the methoxide.

<sup>5</sup>The volume of a methanol molecule (52.4 Å<sup>3</sup>) was calculated from its crystal structure (12).

**TABLE 3**  
Physical Characteristics of  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  and Structural Inferences Drawn

Observation	Structural Information	Reference
Stoichiometry, $\text{MoO}_{5/2}X$	< 3D	(3)
Plate-like morphology	2D	(4)
White color	$\text{MoO}_{3/3}\text{O}_2$ -type chains	(3)
Single line $^{13}\text{C}$ -NMR spectrum	1 type of C atom	(4)

The agreement to within 2% is indeed quite remarkable and suggests the soundness of the above arguments. Finally, if it is assumed that the  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  structure is actually layered, in accord with both the platy habit of the crystallites and the molybdenum atoms positions taken from the structural refinement, then the  $a$ -axis of the methoxide and the  $b$ -axis of the intermediate become the axes associated with the layer stacking direction and are thus a measure of the interlayer spacing ( $IS$ ). If one now takes the volume of a methanol molecule<sup>5</sup> and simply calculates a spherical diameter ( $sd$ ), one has, as yet another check of this developing structure model, the following relationship:

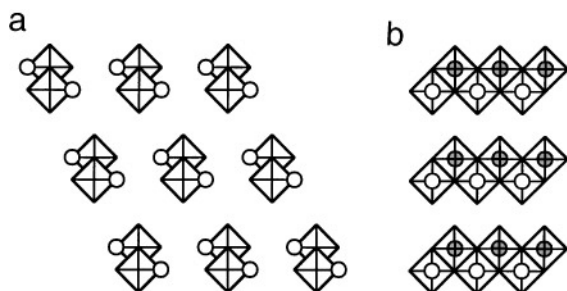
$$IS_{\text{methoxide}} + sd_{\text{methanol}} \approx IS_{\text{intermediate}}$$

$$7.42 + 4.64 \text{ \AA} \approx IS_{\text{intermediate}}$$

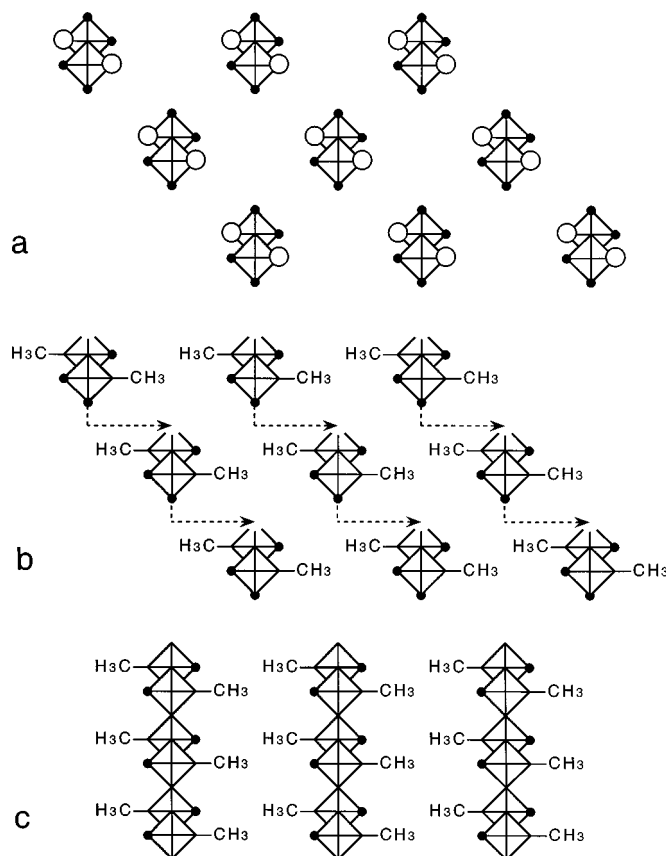
$$12.06 \text{ \AA} \approx 11.66 \text{ \AA}.$$

This is quite reasonable considering that the calculation is most likely an overestimation, since it does not allow for any preferred orientation (of a nonspherical methanol molecule) nor for any nestling of the layers.

It is now possible to combine this crude model of the methoxide structures (i.e., stacked layers of composition  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  and separated by single layers of methanol molecules in the case of  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2 \cdot 2\text{CH}_3\text{OH}$ ) with the reaction chemistry outlined above to propose a structure for the layers themselves.



**FIG. 4.** The crystal structure of white  $\text{MoO}_3 \cdot \text{H}_2\text{O}$  (circles represent  $\text{H}_2\text{O}$ ): viewed (a) parallel to the chain axis and (b) normal to the chains.



**FIG. 5.** Conversion of (a)  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$  via (b)  $\text{H}_2\text{O}$  elimination to give (c) the proposed structure of  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  (open and filled circles represent methanol and singularly coordinated molybdenyl oxygen, respectively).

The fact that a yellow (containing corner-shared octahedral layers) hydrate reacts to form an amorphous white (presumably containing edge-shared octahedral chains) methanolate  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$  (Eq. [1]) implies that a rather substantial structural rearrangement must necessarily take place. Moreover, that it takes place at relatively low temperatures agrees with the observed lack of crystallinity. One speculates in the absence of diffraction data that white  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$  might be a simple structural analog of white  $\text{MoO}_3 \cdot \text{H}_2\text{O}$ <sup>6</sup>, the structure of which is shown in Figure 4.

The loss of water from amorphous  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$  necessary to give the crystalline dimethoxides appears to be a thermally, though relatively mildly so, activated process (Eqs. [2] and [3]). Figures 5 and 6 show how water loss involving two alcoholic protons and the molybdenyl oxygen

<sup>6</sup> It will be of interest to react the white monohydrate with methanol in the hopes of retaining crystallinity via a simple topotactic transformation.

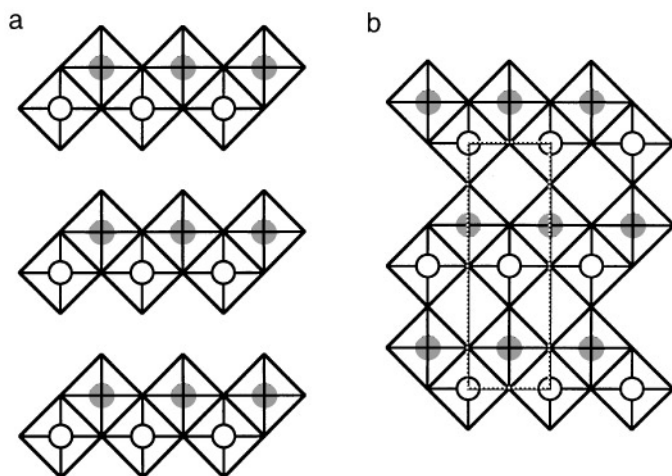


FIG. 6. Conversion of (a)  $\text{MoO}_3 \cdot \text{CH}_3\text{OH}$  to (b)  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  viewed normal to the chain axis (methyl groups represented by circles; proposed unit cell outlined).

*cis* to the methoxide group (the filled circle directed toward the top in Fig. 5)<sup>7</sup> can generate a layered structure for  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  in fair agreement with the observed unit cell parameters. Taking an average *trans*- $\text{MoO}_6$  octahedral distance (*trans*- $d_{\text{oct}}$ ) to be  $\sim 3.9 \text{ \AA}$ <sup>8</sup>, one can generate the following lattice parameters normal to the layer stacking direction for comparison to those found in  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  (see Fig. 6b):

$$3 \text{ trans-}d_{\text{oct}} = 11.7 \text{ \AA} \approx 2 b_{\text{methoxide}} = 12.42 \text{ \AA}$$

$$\text{trans-}d_{\text{oct}} = 3.9 \text{ \AA} \approx c_{\text{methoxide}} = 3.95 \text{ \AA}.$$

That this seemingly reasonable model for the structure of a  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  layer does not fit with the structural refinement of the synchrotron data is an anathema<sup>9</sup>. Besides not being reconcilable with the chemical composition five-coordinate molybdenum as suggested by the structural refinement is exceptionally rare. It is found in only one other solid state oxide structure,  $\text{K}_4\text{MoO}_5$  (11), and in this structure the bipyramidal  $\text{MoO}_5$  moieties are discrete as

<sup>7</sup> Had the *trans*-molybdenyl oxygen been chosen instead, the formation of the resultant one-dimensional structure would necessitate massive structural rearrangement, at odds with both the platy crystal habit and the relatively low temperature of the transformation (Eq. [3]).

<sup>8</sup> The value of  $3.9 \text{ \AA}$  for *trans*- $d_{\text{oct}}$  was derived by averaging the intralayer lattice parameters for  $\alpha\text{-MoO}_3$  (7).

<sup>9</sup> Perhaps part of the problem may be attributable to a high density of defects (discernible as streaking in the electron diffraction pattern (Fig. 3)) which may arise as alluded to in footnote 7 above.

opposed to extended to form a layer. It must therefore be concluded that the truth lies somewhere in all this tangle of data. Fortunately, there are still avenues yet to explore.

## CONCLUSIONS

Based upon numerous physical measurements, reaction chemistry, and a determination of lattice parameters, structures have been proposed for the compounds  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  and  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2 \cdot 2\text{CH}_3\text{OH}$ . Both structures consist of layers of composition  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  and, in the case of the methanolate, separated by a single layer of methanol molecules. The  $\text{Mo}_2\text{O}_5(\text{OCH}_3)_2$  layers are postulated to contain the edge-shared octahedral chains as found in  $\alpha\text{-MoO}_3$  itself. However, the conundrum that this reasonable model does not completely mesh with the model determined using synchrotron diffraction data continues to perplex and confound. We invite any attempt at resolution.

## ACKNOWLEDGMENTS

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