

## The Crystal Structure of $\text{Mo}_4\text{O}_{10}(\text{OH})_2$

KARL-AXEL WILHELM I

*Institute of Inorganic and Physical Chemistry, University of Stockholm, Box 6801,  
S-113 86 Stockholm, Sweden*

$\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , the first member of the series  $\text{MoO}_{3-x}(\text{OH})_x$  with  $x=0.5$ , crystallizes in the orthorhombic system, space group *Cmcm* (No. 63), with the unit-cell dimensions  $a=3.888$  Å,  $b=14.082$  Å, and  $c=3.734$  Å and four formula units in the unit cell. The coordination of the Mo atoms in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  is described as five-fold, *viz.* a square pyramid with Mo-O distances of 1.69 and 1.96 Å. The distance to a sixth oxygen atom completing a very distorted octahedron is as long as 2.33 Å. The bond distances found in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  are compared with those reported in  $\text{MoO}_3$  and  $\text{Mo}_{18}\text{O}_{62}$ .

The existence of a series of molybdenum oxide hydroxides  $\text{MoO}_{3-x}(\text{OH})_x$  ( $0.5 \leq x \leq 2$ ) was first established by Glemser *et al.*<sup>1-4</sup> The X-ray powder patterns indicated close structural relationships with the parent oxide  $\text{MoO}_3$  and led Glemser and Lutz<sup>1</sup> to coin the term *genotypic structures* for this and some analogous families of compounds. The extensive preparative studies included reduction of  $\text{MoO}_3$  in various ways, *viz.* with (a) Zn and HCl, (b) Mo powder and water in sealed glass tubes at 110°C, (c) atomic hydrogen and (d)  $\text{LiAlH}_4$ .

Later on, Kihlberg *et al.*<sup>5</sup> confirmed the existence of the first member of this series *viz.*  $\text{MoO}_{2.5}(\text{OH})_{0.5}$  and proposed the formula  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ . Its powder pattern was indexed assuming an orthorhombic cell, probable space group *Cmcm* (No. 63). It was demonstrated that the substitution of OH groups for oxygen atoms in the structure of  $\text{MoO}_3$  causes a transition to a more ideal structure at least as regards the metal atom arrangements. This was in accordance with previous observations made by Magnéli<sup>6</sup> on the influence of the metal atom valence on the degree of distortion of  $\text{MO}_6$  octahedra in molybdenum and wolfram compounds containing structural elements of  $\text{ReO}_3$  type.

When investigating the system  $\text{MoO}_3-\text{MoO}_2$  at 25 kb, the compound  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  was obtained surprisingly in the form of fairly big crystals. The formation of this material was found to be due to the presence of pyrophyllite in the apparatus which was used as the high pressure medium. This article will describe the structure determination of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ .

## EXPERIMENTAL

The starting materials in this investigation were MoO<sub>3</sub> (Acid Molybdic Anhydride, Reagent grade, Baker and Adamson) and MoO<sub>2</sub> made from MoO<sub>3</sub> by reduction with hydrogen at 500°C.

All experiments were carried out in a girdle high-pressure apparatus constructed at this Institute and described elsewhere.<sup>7</sup> The pressure during all runs was 25 kb. The temperature was kept constant during each run and was measured with a Pt-PtRh thermocouple. The sample tube, which simultaneously served as heating element, was made of platinum and the pressure medium was pyrophyllite. It has been shown by the present author that pyrophyllite gives off hydrogen in the temperature interval 600–1000°C in quantities which can explain the partial reduction of MoO<sub>3</sub> to Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>.

Mixtures of MoO<sub>3</sub> and MoO<sub>2</sub> were heated for about 2 h in the girdle apparatus. For compositions MoO<sub>x</sub> where  $x$  varied between the limits  $3 > x > 2.8$ , it was found that lines of MoO<sub>3</sub> could be detected together with a new pattern of lines. For  $x$  values  $< 2.7$ , the lines of MoO<sub>3</sub> had completely disappeared and new lines originating from MoO<sub>2</sub> were observed. At the composition MoO<sub>2.75</sub>, a single phase seemed to be present which could be identified by means of its X-ray powder pattern as Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>.<sup>8</sup>

The samples consisted of prismatic, rather well developed, black crystals stable in air. The Weissenberg diffraction patterns obtained from apparently single crystals were, however, always multiple, showing the presence of two phases. The composite diffraction patterns showed two orthorhombic lattices, both characterized by distinct diffraction spots, belonging to Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> and MoO<sub>3</sub>. The two individuals in the crystals were orientated so that the  $a$ ,  $b$ , and  $c$  axes of the Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> compound were parallel with the corresponding axes of MoO<sub>3</sub>.

Weissenberg photographs  $hk0-hk2$  and  $0kl-1kl$  were taken with CuK $\alpha$  radiation using a selected crystal which had the approximate dimensions 0.03 mm (distance in the direction of the  $c$  axis)  $\times$  0.01 mm ( $a$ )  $\times$  0.01 mm ( $b$ ). These showed the presence of about 80 % of the Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> and 20 % of the MoO<sub>3</sub> phase, as judged from the intensities of the Weissenberg reflections. No correction for absorption was made.

The values of the cell dimensions of the oxide hydroxide were obtained from an indexed Guinier powder photograph taken with monochromatized CuK $\alpha$  radiation. Potassium chloride ( $a$  (20°C) = 6.2928 Å)<sup>9</sup> was used as an internal standard. The unit cell dimensions were in perfect agreement with those given by Kihlberg *et al.*<sup>8</sup> (Table 1).

Table 1. Crystallographic data for Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>.

Laue symmetry:	$mmm$
Unit cell dimensions:	$a = 3.888 \text{ \AA}$
	$b = 14.082 \text{ \AA}$
	$c = 3.734 \text{ \AA}$
	$V = 204.4 \text{ \AA}^3$
Absent reflections:	$hkl$ with $h+k \neq 2n$
	$h0l$ with $l \neq 2n$
Space group:	No. 63 $Cmcm$

The computational work was performed on the electronic computer FACIT EDB using the following programs: refinement of lattice constants (Program No. 6018), Lorentz-polarization correction (No. 6024), Fourier summations (No. 6015), least squares refinement (No. 6023), and interatomic distances (No. 6016). The numbers refer to the list of crystallographic computer programs.<sup>9</sup> The atomic scattering curves for the neutral atoms were used. The scattering curves<sup>10</sup> were corrected for the real part of the anomalous dispersion.<sup>11</sup>

## STRUCTURE DETERMINATION

The following reflections were found to be systematically missing for Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>:

$$\begin{aligned} hkl & \text{ for } h + k = 2n + 1 \\ h0l & \text{ for } l = 2n + 1 \end{aligned}$$

The systematic absences indicated the choice of space groups: *Cmcm* (No. 63), *C2cm* (No. 40), and *Cmc2<sub>1</sub>* (No. 36).

The structure determination was started on the assumption that the structure has a centre of symmetry, *i.e.* the space group is *Cmcm* (No. 63).

The space group of MoO<sub>3</sub> in *Pbnm* (No. 62 in an alternative orientation) with the atoms in four-fold positions 4(c):  $xy\frac{1}{4}$ ;  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}$ ;  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{4}$ ;  $\bar{x}, \bar{y}, \frac{3}{4}$ . A least squares refinement of MoO<sub>3</sub> performed by Kihlberg<sup>12</sup> has given the following parameter values:

	<i>x</i>	<i>y</i>
Mo	0.08669	0.10164
O(1)	0.0006	0.93513
O(2)	-0.0212	0.58657
O(3)	0.0373	0.22140

A *C*-centering of the MoO<sub>3</sub> lattice can be achieved if the four *x*-coordinates of the trioxide are put equal to zero. In *Cmcm* (No. 63) the following point positions exist:

$$\begin{aligned} & (0,0,0; \frac{1}{2}, \frac{1}{2}, 0) + \\ 4(a) & 0,0,0; 0,0, \frac{1}{2} & 8(e) & x,0,0; \bar{x},0,0; x,0, \frac{1}{2}; \bar{x},0, \frac{1}{2} \\ 4(b) & 0, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2} & 8(f) & 0,y,z; 0,\bar{y},\bar{z}; 0,y, \frac{1}{2}-z; 0,\bar{y}, \frac{1}{2}+z \\ 4(c) & 0,y, \frac{1}{4}; 0,\bar{y}, \frac{3}{4} & 8(g) & x,y, \frac{1}{4}; \bar{x},y, \frac{1}{4}; x,\bar{y}, \frac{3}{4}; \bar{x},\bar{y}, \frac{3}{4} \\ 8(d) & \frac{1}{4}, \frac{1}{4}, 0; \frac{1}{4}, \frac{3}{4}, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{2}; \frac{1}{4}, \frac{3}{4}, \frac{1}{2} & 16(h) & \pm(x,y,z; x,\bar{y},\bar{z}; x,y, \frac{1}{2}-z; x,\bar{y}, \frac{1}{2}+z) \end{aligned}$$

As can be seen, only 4(c) in this space group can accommodate the molybdenum and oxygen atoms and it was tentatively assumed that the atoms in Mo<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> are placed in 4(c) in the space group *Cmcm* and the *y*-coordinates given above for MoO<sub>3</sub> were used as the starting parameters for the least squares refinement. All 134 of the independent observed reflections were included in the calculations.

The structure factors were weighted by Cruickshank's weighting function:

$$w = (a + |F_o| + b|F_o|^2)^{-1}$$

The refinement was considered complete when the successive shifts were well below 5 % of the standard deviations at which point the discrepancy index, *R*, was down to 0.110. A weight analysis obtained in the last cycle is given in Table 2.

Table 2. Weight analysis obtained in the final cycle of the least squares refinement of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ .  $w$  = weighting factor  $\Delta = ||F_o| - |F_c||$ .

Interval $\sin \theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval $F_o$	Number of independent reflections	$\overline{w\Delta^2}$
0.00—0.46	21	0.70	0—10	6	3.18
0.46—0.58	14	1.20	10—20	19	0.65
0.58—0.67	18	0.92	20—30	23	0.77
0.67—0.74	12	0.78	30—40	21	0.97
0.74—0.79	13	1.21	40—50	17	0.96
0.79—0.84	12	0.37	50—60	12	0.96
0.84—0.89	18	1.66	60—70	9	1.09
0.89—0.93	9	1.65	70—80	9	0.69
0.93—0.96	11	0.81	80—90	6	1.19
0.96—1.00	6	0.46	90—100	12	0.68

Table 3. The structure of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ . Final coordinates, isotropic temperature factors and standard deviations as obtained from the least squares refinement.

Space group:  $Cmcm$  (No. 63)

$(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) +$

All atoms in  $4(c) \pm(0, y, \frac{1}{2})$

	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B) \text{ \AA}^2$
4 Mo	0	$0.1035 \pm 2$	1/4	$1.80 \pm 7$
4 O(1)	0	$0.9379 \pm 28$	1/4	$2.66 \pm 70$
4 O(2)	0	$0.5865 \pm 18$	1/4	$0.45 \pm 39$
4 O(3)	0	$0.2233 \pm 20$	1/4	$1.24 \pm 48$

The final fractional atomic parameters obtained and their standard deviations  $\sigma$  are shown in Table 3 as well as the refined thermal parameters.

A three-dimensional difference synthesis was computed over the asymmetric unit of the structure cell. The largest maxima and minima in this synthesis are less than about 25 % of the mean oxygen peak height in the electron density function. The observed and calculated structure factors are given in Table 4.

The essential correctness of the hypothetical structure was verified by this procedure.

Among the three possible space groups  $Cmcm$  (No. 63),  $C2cm$  (No. 40), and  $Cmc2_1$  (No. 36), the latter two are non-centrosymmetric. The refinement was continued in these two alternative space groups using the procedure described by Åsbrink and Kihlberg.<sup>13</sup> The coordinates thus obtained did not differ significantly from the values found for the centrosymmetrical space group which was taken as the actual symmetry of the compound.

The interatomic distances and bond angles are given in Table 5. The arrangement of the atoms is shown in Fig. 1b.

Table 4. Comparison between calculated and observed structure factors from Weissenberg photographs of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ .  $\text{CuK}\alpha$  radiation.

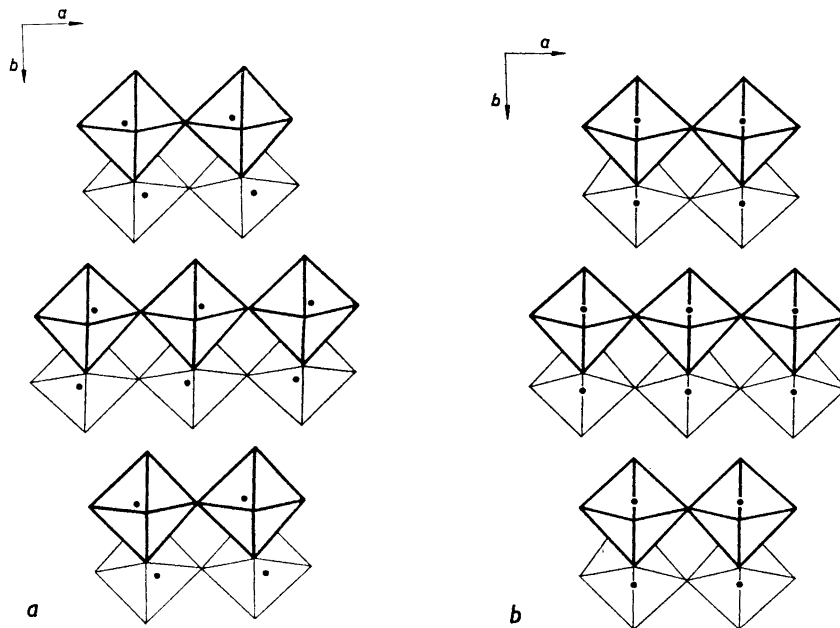
$h$	$k$	$l$	$F_o$	$ F_c $	$h$	$k$	$l$	$F_o$	$ F_c $
2	0	0	155	159	1	5	1	16	22
4	0	0	74	71	1	7	1	77	93
0	2	0	52	47	1	9	1	17	17
0	4	0	97	110	1	11	1	72	63
0	6	0	133	132	1	13	1	50	40
0	8	0	26	31	1	15	1	15	15
0	10	0	90	84	1	17	1	52	43
0	12	0	15	10					
0	14	0	52	43	2	2	1	112	103
0	16	0	31	31	2	4	1	32	38
0	18	0	27	24	2	6	1	59	55
					2	8	1	73	83
1	1	0	123	116	2	10	1	15	18
1	3	0	52	49	2	12	1	60	53
1	5	0	93	89	2	14	1	29	27
1	7	0	31	30					
1	9	0	85	78	3	1	1	36	44
1	11	0	32	24	3	3	1	33	39
1	13	0	45	32	3	5	1	11	11
1	15	0	52	43	3	7	1	67	57
					3	9	1	8	11
2	2	0	31	31	3	11	1	44	41
2	4	0	76	81	3	13	1	33	27
2	6	0	84	91					
2	8	0	29	26	4	2	1	53	53
2	10	0	69	67	4	4	1	15	22
2	12	0	10	8	4	6	1	23	29
2	14	0	36	35	4	8	1	46	46
2	16	0	30	27					
					0	2	2	23	30
3	1	0	52	59	0	4	2	78	79
3	3	0	29	28	0	6	2	99	90
3	5	0	44	54	0	8	2	26	26
3	7	0	12	15	0	10	2	74	66
3	9	0	52	51	0	12	1	9	8
3	11	0	4	16	0	14	2	44	35
3	13	0	28	23	0	16	2	27	27
4	2	0	11	14	1	1	2	82	78
4	4	0	38	42	1	3	2	36	35
4	6	0	42	46	1	5	2	70	67
4	8	0	10	15	1	7	2	22	20
4	10	0	41	39	1	9	2	66	61
					1	11	2	26	20
0	2	1	132	143	1	13	2	28	26
0	4	1	50	47	1	15	2	39	35
0	6	1	83	74	2	0	2	115	112
0	8	1	118	110	2	2	2	24	23
0	10	1	22	24	2	4	2	64	62
0	12	1	72	65	2	6	2	70	69
0	14	1	29	32	2	8	2	21	21
0	16	1	40	33	2	10	2	48	54
					2	12	2	4	7
1	1	1	80	78	2	14	2	32	29
1	3	1	62	52					

Table 4. Continued.

<i>h k l</i>	$F_o$	$ F_c $	<i>h k l</i>	$F_o$	$ F_c $
3 1 2	42	46	1 5 4	35	34
3 3 2	21	22	1 7 4	10	8
3 5 2	41	44	1 9 4	32	33
3 7 2	12	11			
3 9 2	38	41	0 2 3	75	77
3 11 2	16	13	0 4 3	30	31
			0 6 3	44	42
4 0 2	42	58	0 8 3	65	64
4 2 2	8	12	0 10 3	15	14
4 4 2	30	35	0 12 3	46	42
4 6 2	30	38	0 14 3	23	22
1 1 3	40	42	0 2 4	14	14
1 3 3	35	38	0 4 4	40	40
1 5 3	12	11	0 6 4	46	43
1 7 3	56	55	0 8 4	12	14
1 9 3	11	12	0 10 4	38	37
1 11 3	44	40			
			0 0 2	157	154
1 1 4	38	35	0 0 4	68	67
1 3 4	18	18			

Table 5. Interatomic distances and angles in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ .

Mo—Mo distances ( $\sigma \approx 0.005 \text{ \AA}$ )	O—O distances ( $\sigma \approx 0.06 \text{ \AA}$ )
Mo—Mo	3.462 $\text{ \AA}$
Mo—Mo $_{  }$ [001]	3.734
Mo—Mo $_{  }$ [100]	3.888
Mo—O distances ( $\sigma \approx 0.03 \text{ \AA}$ )	O(1)—O(1')
Mo—O(1)	$2 \times 2.558 \text{ \AA}$
Mo—O(1')	2.856
Mo—O(2)	1.959
Mo—O(2')	1.959
Mo—O(3)	1.687
$\angle \text{O—Mo—O}$ ( $\sigma \approx 1^\circ$ )	O(1)—O(2)
O(1)—Mo—O(1')	$2 \times 2.717$
O(1)—Mo—O(2)	$2 \times 2.717$
O(1)—Mo—O(2')	$2 \times 2.939$
O(1)—Mo—O(3)	180
O(1')—Mo—O(1')	145
O(1)—Mo—O(2)	$2 \times 88$
O(1)—Mo—O(2')	$2 \times 88$
O(1')—Mo—O(3)	$2 \times 107$
O(2)—Mo—O(2')	166
O(2)—Mo—O(3)	97
O(2')—Mo—O(3)	97
	O(1)—O(3)
	$2 \times 2.737$
	O(2)—O(3')
	$2.737$
	O(2)—O(3'')
	$3.265$
	O(3)—O(1)
	$2 \times 2.939$
	O(3)—O(2)
	$2.737$
	O(3)—O(2')
	$2.737$
	O(3)—O(2'')
	$2 \times 3.265$
	O(3)—O(3')
	$4 \times 2.798$



*Fig. 1.* The crystal structures of  $\text{MoO}_3$  (a) and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  (b) represented in terms of the octahedra, which are obtained by joining the centres of the oxygen atoms coordinated with each metal atom. Octahedra indicated by heavy lines are situated at a higher level than those drawn with thin lines. The positions of the molybdenum atoms within the octahedra are marked with black dots.

The temperature factors of the oxygen atoms diverged and the final values range from 0.45 to 2.66 Å<sup>2</sup> (mean 1.45 Å<sup>2</sup>). The same effect was observed by Kihlberg in the refinement of  $\text{Mo}_{18}\text{O}_{52}$ <sup>14</sup> and was interpreted as arising from the systematic errors introduced by extinction effects and the moderate accuracy of the intensity data.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of  $\text{MoO}_3$  represents a transitional stage between octahedral and tetrahedral coordination as shown by Kihlberg<sup>12</sup> with a strong tendency towards four-fold coordination. In the structure of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , the tendency towards a more ideal octahedral configuration of the O atoms around the Mo atoms is obvious (*cf.* Fig. 2a—b); the Mo atoms have five oxygen neighbours at distances ranging from 1.69 to 1.96 Å while the distance to the remaining sixth oxygen atom which completes the octahedron is as long as 2.33 Å. Accordingly, the coordination in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  is best described as five-fold.

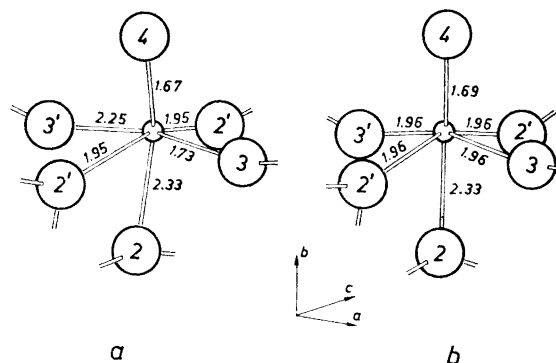


Fig. 2. The coordination of oxygen atoms (large spheres) around the molybdenum atoms (small spheres) in  $\text{MoO}_3$  (a) and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  (b). (The numbering of the atoms is in accordance with Ref. 12).

The crystal structure of  $\text{Mo}_{18}\text{O}_{52}$  has been determined by Kihlberg.<sup>14</sup> It has a basic structure of  $\text{MoO}_3$  type which forms slabs infinite in two dimensions. These slabs are connected by a complicated shear mechanism.

The Mo—Mo and Mo—O distances in  $\text{MoO}_3$  and the mean values for the distances within the interior of the basic strings of  $\text{Mo}_{18}\text{O}_{52}$  as calculated by Kihlberg, together with the corresponding distances in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , are given in Table 6.

As can be seen from this table, the interatomic distances within the basic slabs of  $\text{Mo}_{18}\text{O}_{52}$  are almost the same as in  $\text{MoO}_3$ . The Mo—Mo separations along [100] and [001], viz. in the plane of the layers, are both greater and less, respectively, for  $\text{Mo}_{18}\text{O}_{52}$  and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  than those for  $\text{MoO}_3$  and these changes are associated with a considerable reduction in the distortion of the octahedra. The length of the *b* axis, which corresponds to twice the value of the interlayer separation, is for  $\text{MoO}_3$ , 13.855 Å;  $\text{Mo}_{18}\text{O}_{52}$ , 14.46 Å; and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , 14.082 Å. The lattice expansion, reflected in the length of the

Table 6. Comparison between the interatomic distances (in Å) in  $\text{MoO}_3$  (Ref. 12) the mean values for the distances in the basic structure of  $\text{Mo}_{18}\text{O}_{52}$  (Ref. 14) and the corresponding distances in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  (cf. Fig. 2 a, b).

Distance in $\text{MoO}_3$	$\text{MoO}_3$	$\text{Mo}_{18}\text{O}_{52}$	$\text{Mo}_4\text{O}_{10}(\text{OH})_2$
Mo—Mo across shared edges	3.438	3.427	3.462
Mo—Mo along [100]	3.963	3.837	3.888
Mo—Mo along [001]	3.696	3.734	3.734
Mo—O A	1.671	1.673	1.69
B	1.948	1.955	1.96
C	1.948	1.955	1.96
D	2.332	2.340	2.33
E	1.734	1.799	1.96
F	2.251	2.121	1.96



$b$  axis, is mainly due to the more ideal octahedral arrangement and is much more pronounced for  $\text{Mo}_{18}\text{O}_{52}$  (see below).

The mean values of the O—O separations in the compound  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  are (the corresponding values for  $\text{MoO}_3$  within brackets): for the O(1) atoms, 2.76 Å (2.75); O(2), 2.89 Å (2.89); and O(3), 2.91 Å (2.89). The density of the anion packing, expressed in terms of the quotient  $V/n_{\text{O}}$  ( $V$ =volume of the unit cell in Å<sup>3</sup>,  $n_{\text{O}}$ =number of oxygen atoms) is for the following compounds:  $\text{MoO}_3$ , 16.2;  $\text{MoO}_3$ , 16.9; and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , 17.0. The rather low values indicate a fairly close-packed oxygen arrangement in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  which is also reflected in high coordination numbers of oxygen atoms around themselves; the distance ranges and coordination numbers for the various atoms being: O(1), 2.56–2.94 Å, 10; O(2), 2.72–3.27 Å, 12; O(3), 2.74–3.27 Å, 10. The displacements of the oxygen atoms when going from the  $\text{MoO}_3$  structure to  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  are comparatively small — the maximum shift in the O—O distances does not exceed 0.1 Å. Thus it is obvious that no conclusions can be drawn from a comparison of these distances in the two compounds as regards to the positions of the hydrogen atoms in the structure of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ . However, the most likely place of the hydrogen atoms is between the sheets and this opinion is supported by the fact that the increase in the interlayer distance observed in  $\text{Mo}_{18}\text{O}_{52}$  and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , which is mainly due to the idealization of the  $\text{MoO}_6$  octahedra, is much less pronounced for the latter compound (see above).

There are six interlayer oxygen-oxygen contacts: four distances between the O(3)—O(3) atoms of length 2.80 Å and two distances between the O(3)—O(2) atoms of 3.26 Å. The former value is reasonable for a hydrogen bond but the latter is far too large for such a bond. As hydrogen has no other likely place in the structure, the conclusion must be drawn that two hydrogen atoms in the unit cell are placed in some way between the O(3) atoms belonging to two different layers.

It was made clear in the work of Evans *et al.*<sup>15–18</sup> on hydrated vanadium oxide minerals that localized ordering of the hydrogen atoms is not confined to anhydrous materials prepared by fusion methods. The existence of a series of discrete oxide hydroxide phases  $\text{MoO}_{3-x}(\text{OH})_x$  ( $x=0.5, 1.0, 1.6,$  and  $2.0$ ) makes it very possible that the hydrogen atoms in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  ( $x=0.5$ ) are also ordered in some way.

Because of the favourable scattering factors of hydrogen and deuterium relative to those of the metal atoms, neutron diffraction has provided most of the accurate information concerning the location of hydrogen atoms in crystals. Rather few works with this technique have been reported in literature concerning oxide hydroxides and especially in the case of transition metal compounds.<sup>19</sup> An investigation of  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$  with this technique appears highly desirable and a neutron diffraction study of the deuterated compound in order to obtain detailed knowledge about the arrangement of the hydrogen atoms has been started.

## REFERENCES

1. Glemser, O. and Lutz, G. *Z. anorg. allgem. Chem.* **264** (1951) 17.
2. Glemser, O., Hauschild, U. and Lutz, G. *Z. anorg. allgem. Chem.* **269** (1952) 93.
3. Glemser, O. *Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl., Abt. IIa* (1955) 121.
4. Glemser, O., Lutz, G. and Meyer, G. *Z. anorg. allgem. Chem.* **285** (1956) 173.
5. Kihlborg, L., Hägerström, G. and Rönquist, A. *Acta Chem. Scand.* **15** (1961) 1187.
6. Magnéli, A. *J. Inorg. Nucl. Chem.* **2** (1956) 330.
7. Daniels, W. B. and Jones, M. T. *Rev. Sci. Instr.* **32** (1961) 885; Wilhelmi, K.-A. and Burger, W. *Acta Chem. Scand.* **23** (1969) 414.
8. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
9. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., A. Oosthoek's Uitgevers Mij. N.V., Utrecht 1966.
10. Hanson, H. P., Herman, F., Lea, I. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
11. Dauben, C. H. and Templeton, D. H. *Acta Cryst.* **8** (1955) 841.
12. Kihlborg, L. *Arkiv Kemi* **21** (1963) 357.
13. Åsbrink, S. and Kihlborg, L. *Acta Chem. Scand.* **18** (1964) 1571.
14. Kihlborg, L. *Arkiv Kemi* **21** (1963) 443.
15. Evans, H. T. and Block, S. *Am. Mineralogist* **38** (1953) 1242.
16. Evans, H. T. and Moore, M. E. *Am. Mineralogist* **40** (1955) 861.
17. Evans, H. T. and Moore, M. E. *Acta Cryst.* **11** (1958) 56.
18. Evans, H. T. and Moore, M. E. *Am. Mineralogist* **45** (1960) 1144.
19. Dickens, P. G. and Hurditch, R. J. *Nature* **215** (1967) 1266.

Received June 19, 1968.