

## A Study of the Crystal Symmetry and Structure of Orthorhombic $\text{Mo}_4\text{O}_{11}$ by Least-squares Techniques

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In connection with the determination of the crystal structure of the monoclinic, low-temperature form of  $\text{Mo}_4\text{O}_{11}$ , recently reported by one of the present authors,<sup>1</sup> a partial least-squares refinement was also carried out of the structure of the orthorhombic, high-temperature modification of this compound, originally determined by Magnéli<sup>2</sup> in 1948. This refinement was based on 1280 independent intensities estimated from Weissenberg photographs. A final  $R$ -value of 0.084 was obtained and the estimated standard deviations in the coordinates were 0.0017 Å for the Mo atoms and 0.010–0.017 Å for the O atoms, which was considered fairly satisfactory. (Almost the same values, *viz.* 0.078, 0.0016 Å, 0.014 Å, respectively, were obtained for the monoclinic form.) The values obtained for the isotropic temperature factors were quite normal for the metal atoms ( $B = 0.29 - 0.36 \text{ \AA}^2$ ) but showed rather large divergence for the oxygen atoms ( $B = 0.75 - 2.91 \text{ \AA}^2$ ). In particular, the  $B$ -values were suspiciously high for two of the oxygen atom positions. Some tests were made to reveal the reason for this but these did not give any positive answer to the question, and the conclusion was drawn that the origin of these anomalous values was to be sought in systematic errors of some kind. The possibility of the structure possessing a lower space-group symmetry was, however, not investigated at this stage. In connection with investigations of the applicability of least-squares methods to reveal minor deviations from centrosymmetry in crystal structures, a further structural refinement of orthorhombic  $\text{Mo}_4\text{O}_{11}$  was found worthwhile and will be described below.

The observed systematic absences of reflections are characteristic of the space groups  $Pnma$  and  $Pn2_1a$ , the latter being non-centrosymmetric. With the methods available when the original structure determination of this phase was carried out it

was not possible to decide between these two cases. It was found, however, that the structure could be satisfactorily described in the centrosymmetrical space group  $Pnma$ .<sup>2</sup> This space group assumption was retained in the previous refinement referred to above.<sup>1</sup> The refinement has now been continued in the alternative space group  $Pn2_1a$ .

The atomic parameters given in Table 3 of Ref.<sup>1</sup> formed the basis for the continued refinement. In the space group  $Pnma$  the atoms were placed in the special point positions 4( $a$ ) and 4( $c$ ) and in the general position 8( $d$ ). There is only one type of position in  $Pn2_1a$ , namely the 4-fold position 4( $a$ ). The 8-fold position in  $Pnma$  occupied by the oxygen atoms Nos. 6, 7, and 8 each corresponds to pairs of 4-fold positions, and these are designated 6' and 6'' etc. in this paper. The rest of the atoms which occupied special positions in  $Pnma$  had one (atoms Nos. 1–4, 9–12) or three (atom No. 5) coordinates fixed by reason of symmetry. All these coordinates are variable in the new space group.

The same block-diagonal least-squares program<sup>3</sup> was used as in the previous refinement. Because of the symmetry inherent in the starting coordinates it was not possible to start the computation by refining all the coordinates. The following procedure was used in sequence.

1. The coordinates refined previously were first refined with the exception of those of the atoms 6'', 7'', and 8'' which were kept constant. In this way the centrosymmetric relationship within the pairs 6'–6'', 7'–7'', and 8'–8'' was removed (5 cycles).

2. In the next step the coordinates of 6'', 7'' and 8'' were released (2 cycles).

3. After that, the  $y$  coordinates of the four Mo atoms were set free (4 cycles).

4. The coordinates still kept fixed (all the coordinates of atom 5 and the  $y$  coordinates of atoms 9–12) were then released and all parameters were varied (10 cycles).

After this, the refinement was considered complete since no shift was larger than 0.03  $\sigma$  ( $\sigma =$  standard deviation) and no parameter was creeping in the last cycles. The  $R$ -value decreased from 0.084 to 0.062 by this refinement. The finally obtained parameters and their standard deviations are given in Table 1. The origin of the unit cell is not fixed by symmetry in the [010] direction. In the present case it has been chosen so that the mean value of

Table 1. The crystal structure of  $\text{Mo}_4\text{O}_{11}$  (orthorhombic). Space group:  $Pn2_1a$  (No. 33 of *International Tables* in an alternative orientation). Unit-cell dimensions (\*):  $a = 24.49 \text{ \AA}$ ,  $b = 5.457 \text{ \AA}$ ,  $c = 6.752 \text{ \AA}$ . Cell content: 4  $\text{Mo}_4\text{O}_{11}$ , 16 Mo and 44 O in  $4 \times 4(a)$ :  $(x, y, z)$ ;  $\bar{x}, \frac{1}{2} + y, \bar{z}$ ;  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ;  $\frac{1}{2} + x, y, \frac{1}{2} - z$ .

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
Mo 1	$0.20535 \pm 0.00005$	$0.2638 \pm 0.0004$	$0.87214 \pm 0.00018$	$0.340 \pm 0.013$
2	.14690 .00005	.7419 .0004	.19715 .00018	0.245 .011
3	.08714 .00005	.2477 .0005	.52144 .00018	0.316 .012
4	.02852 .00006	.7466 .0005	.84123 .00020	0.351 .011
O 5	.9979 .0007	.9766 .0028	.0112 .0026	0.45 .15
6'	.0608 .0006	.0203 .0026	.6849 .0021	0.69 .18
6''	.9326 .0007	.0141 .0029	.3365 .0023	1.05 .22
7'	.1247 .0006	.9702 .0028	.3603 .0021	0.63 .18
7''	.8712 .0006	.9685 .0029	.6815 .0021	0.66 .19
8'	.1872 .0006	.0356 .0028	.0387 .0023	0.83 .20
8''	.8064 .0006	.0499 .0028	.0138 .0022	0.80 .20
9	.0309 .0005	.2567 .0045	.3425 .0017	0.70 .13
10	.0943 .0005	.7648 .0040	.0179 .0017	0.75 .16
11	.1645 .0005	.2379 .0035	.6593 .0018	0.89 .16
12	.2240 .0005	.7318 .0035	.3203 .0018	1.00 .19

the  $y$  coordinates for the metal atoms remain unchanged compared with the coordinates previously given.

It is evident that  $Pn2_1a$  is the most correct space group in the present case. All anomalies in the temperature factors have disappeared, as is seen in Table 1.

The difference between the new atomic positions and those reported in Ref.<sup>1</sup> is largest for the oxygen atoms 8', 8'', and 7', viz., 0.31, 0.27, and 0.28 Å, respectively. It falls within the range 0.1–0.2 Å for the atoms 5, 6', 6'', and 7' and is less than 0.1 Å for the rest of the atoms. The largest changes are generally observed for the  $y$  coordinates. The general features of the structure remain unchanged, however, and the description previously given is still valid.

The new Mo–O distances are listed in Table 2, together with the values reported previously (Ref.<sup>1</sup>, Table 5). The changes are seen to be greatest for the distances 2–7'' (+0.051 Å), 2–8' (+0.051 Å), 2–7' (+0.042 Å) and 1–8'' (+0.038 Å), but are rather small for most distances. With few exceptions the values have become more equal to those obtained for the corresponding distances in the monoclinic, low-temperature form of  $\text{Mo}_4\text{O}_{11}$ .<sup>1</sup> The close similarity between these two structures as regards the coordination around the molybdenum atoms, pointed out in Ref.<sup>1</sup>, has thus become still more pronounced.

Table 2. Mo–O distances. The values previously given<sup>1</sup> are within parentheses. The standard deviations in the distances are about  $\pm 0.017 \text{ \AA}$ .

Atoms	Distance (Å)
1–12	1.775 (1.757)
1–8'	1.736 (1.725)
1–8''	1.763 (1.725)
1–11	1.756 (1.738)
2–12	2.063 (2.064)
2–8'	2.164 (2.113)
2–8''	2.107 (2.113)
2–7'	1.750 (1.708)
2–7''	1.759 (1.708)
2–10	1.772 (1.760)
3–11	2.112 (2.122)
3–7'	2.079 (2.105)
3–7''	2.090 (2.105)
3–6'	1.781 (1.780)
3–6''	1.807 (1.780)
3–9	1.832 (1.817)
4–10	2.007 (2.011)
4–6'	1.993 (1.990)
4–6''	1.989 (1.990)
4–9	1.913 (1.929)
4–5	1.893 (1.871)
4–5	1.858 (1.871)

It has been shown<sup>1,5</sup> that if, for each oxygen atom bonded to two molybdenum atoms, the sum of the two Mo-O distances are plotted against the difference between these, the points fall close to one and the same curve for all molybdenum oxides for which accurate atomic distances are known. Some points corresponding to distances in Mo<sub>4</sub>O<sub>11</sub> (o-rh.) showed the greatest deviation from this curve. Calculated from the new values of interatomic distances these points fit to the curve much better.

It was also found previously<sup>5</sup> that a logarithmic relation, according to Pauling, between bond distance and bond number could be formulated which corresponds to the above-mentioned curve assuming that the sum of bond numbers to each oxygen atom is 2. With the aid of this formula the sum of the bond numbers was calculated for the metal atoms in some molybdenum oxides. A systematic variation in the values thus obtained was observed for Mo<sub>8</sub>O<sub>23</sub>, Mo<sub>4</sub>O<sub>11</sub> (mon.) and Mo<sub>4</sub>O<sub>11</sub> (o-rh.). Rather high values were, however, obtained for the atoms 1 and 2 in the last of these structures, viz., 6.40 and 6.36, respectively, compared to an expected maximum value of 6. Calculations based on the new interatomic distances give the values 5.94, 5.74, 5.17, and 4.80 for the atoms 1, 2, 3, and 4, respectively, (mean value 5.41, expected 5.50), which are all below the expected maximum and close to the corresponding values calculated for the monoclinic form.

A complete list of interatomic distances and angles in this structure as well as the observed and calculated structure factors is given in a separate document<sup>6</sup> copies of which may be obtained on request from the secretary of this institute.

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## Mass Spectra and Organic Analysis IV<sup>1</sup> Some Comments on the Mass Spectra of Monoterpene Alcohols

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A recent publication of the mass spectra of some monoterpene alcohols<sup>2</sup> which were obtained by a method which we have already criticized<sup>1</sup> has led us to examine the differences between our results and those of the Swedish group in more detail.

As we have mentioned,<sup>2</sup> the main differences between the methods are in the energy of the bombarding electrons (70 eV in our case and 20 eV in the Swedish work<sup>3</sup>) and the presence of a large amount of helium with the sample in the latter case. The first of these differences accounts for the higher proportion of light fragments (particularly below *m/e* 60) that we observe, and is illustrated in Figs. 1 and 2 (linalool) and Figs. 3 and 4 (sabinol), which we measured at both 20 eV (Figs. 1 and 3) and 70 eV (Figs. 2 and 4). This, however, is not sufficient to explain all the differences observed. In the case of linalool, for instance, von Sydow shows fragments of significantly greater intensity at *m/e* 155, 93, 68, 67, and 59, and his fragments at *m/e* 43 and 41 would fit better with bombarding electrons at 70 eV rather than 20 eV. We considered at first the possibility of reaction of He<sup>+</sup> ions with the substance under examination, but we could detect no difference in our spectra even when measured in the presence of a 4-fold excess of helium. Since only