

*Acta Cryst.* (1976). A32, 342

**Contributions to the chemistry of Mo and W. XVIII.\* The structures of the triclinic and orthorhombic modifications of  $\text{WO}_3$ .** By F. A. SCHRÖDER, *Gmelin-Institut für Anorganische Chemie der Max-Planck-Gesellschaft, D-6 Frankfurt/M. 90, Varrentrappstr. 40/42, Deutschland (BRD)*

(Received 31 July 1975; accepted 12 November 1975)

The structure of the triclinic modification of  $\text{WO}_3$  in terms of the  $\text{O} \rightarrow \text{W}$  electric dipoles is proposed. In the same way, based on the relationships with the structures of  $\text{MoO}_3$  and  $\text{WO}_2\text{Cl}_2$ , the structure of the orthorhombic modification of  $\text{WO}_3$  is proposed.

**(a) Triclinic  $\text{WO}_3$**

Van Landuyt & Amelinckx (1969) first showed that the model of electric dipoles for the long  $\text{O} \rightarrow \text{W}$  bonds is used very successfully to explain the well known (100) domains in monoclinic  $\text{WO}_3$ . Schröder & Hartman (1972) discussed the problem thoroughly, considering all existing chains of electric dipoles (along [100] and [001]). The result is that in the structure section  $d_{002}$  of the monoclinic unit cell both types of chains (two from each) are arranged corresponding to a minimum of repulsion that is mutually antiparallel. The second section  $d_{002}$  is (because there are two independent formula units in monoclinic  $\text{WO}_3$ ) quasi-translational with respect to the first one. This leads to a total of two parallel [010] dipole chains on the common (002) face. This boundary repulsion is obviously low enough for the unit cell to exist while a total of four parallel dipole chains (two [010] and two [001]) at the (100) boundary leads to the (100) domain growth [cf. Fig. 5 in Schröder & Hartman (1972)]. Schröder (1973) postulated the existence of another  $\text{WO}_3$  unit cell of nearly the same size, which is derived formally from the known form by rotation of the [010] chains (this means the  $\text{WO}_3$  octahedra) by  $180^\circ$  around the [001] dipole chain 'axis'. This unit cell is shown in Fig. 1 and is here attributed to one of the suggested low-temperature modifications of  $\text{WO}_3$ :

Taking into account the very recent investigations on this subject [Salje, 1974; Salje & Viswanathan, 1975; Salje, 1975, hereafter referred to as S. (1974), S. & V. (1975) and S. (1975)] it is supposed that this derived unit cell is that of the triclinic structure,  $\text{WO}_3(\text{II})$  according to S. & V. (1975). This is supported by the following points:

(1) Because of the lack of internal repulsion from parallel dipole chains, the volume of the derived unit cell should be smaller than that of the monoclinic unit cell. This has been confirmed:  $421.8$  (2) instead of  $422.8$  (2)  $\text{\AA}^3$  (S. & V., 1975). The volume has been doubled for both cells since from experience of X-ray powder data of monoclinic  $\text{WO}_3$ , it is known that  $C=c/2$  is always obtained by this method.

(2) The derived triclinic cell would be space group  $P1$  which allows ferroelectric or antiferroelectric behaviour, observed several times, contrary to the known centrosymmetric monoclinic space group.

(3) The only noticeable difference between the lattice parameters of monoclinic and triclinic  $\text{WO}_3$  is found to be a contraction in  $b$ . It may be concluded that the short  $\text{W}-\text{O}_y$  ( $\pi$ -bonding) distances are shortened from an average of  $1.763$   $\text{\AA}$  to approach the  $\text{W}-\text{O}_z$  distances (av.  $1.736$   $\text{\AA}$ ).

**(b) Orthorhombic  $\text{WO}_3$**

Schröder & Felser (1972) described crystals of monoclinic  $\text{WO}_3$  showing (100) domains. The X-ray pattern showed reflexions  $hk0$ :  $k=2n+1$  only, after long exposures of Weissenberg photographs. Later Schröder (1973), from this orthorhombic pseudosymmetry, concluded that the space group of the orthorhombic  $\text{WO}_3$  should be  $Pmnb$  (Standard:  $Pnma$ ). The same result was obtained recently (S. & V., 1975). This is the same space group shown by the usual orthorhombic structure of  $\text{MoO}_3$ , although this structure was solved in an alternative orientation, namely  $Pbmn$  [Last refinement Kihlberg (1963/4)]. From this information the structure of orthorhombic  $\text{WO}_3$  may be predicted and demonstrate the influence of dipole chains in systemizing the modifications of  $\text{WO}_3$ . Table 1 shows the hitherto measured lattice parameters of orthorhombic  $\text{WO}_3$ . The most recent values show satisfactory agreement. The lattice parameters of  $\text{MoO}_3$  according to Kihlberg (1963/4), in the orientation  $Pmnb$  are included in Table 1. It is seen that  $2a$  ( $\text{MoO}_3$ )  $\approx a$  (o'r.h.  $\text{WO}_3$ ),  $b$  ( $\text{MoO}_3$ )  $\sim 2b$  (o'r.h.  $\text{WO}_3$ ) and  $c$  ( $\text{MoO}_3$ )  $\approx c$  ( $\text{WO}_3$ ). While the agreements for  $a$  and  $c$  are satisfactory, there is a difference of  $7.570-6.927-0.643$   $\text{\AA}$  in  $b$ .

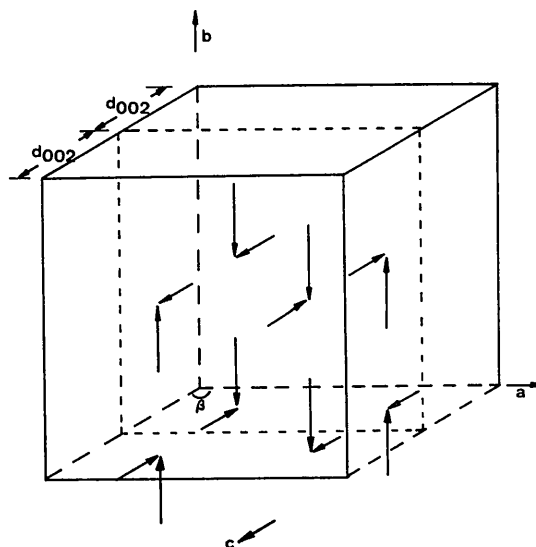


Fig. 1. The proposed unit cell of triclinic  $\text{WO}_3$ . The described rotation has been carried out on the  $d_{002}$  section in the front of the figure.

\* For part XVII see *Z. Naturforsch.* (1975). B30, 638.

Fig 2 shows the structure of orthorhombic  $\text{WO}_3$  by the usual idealized octahedra. The axes are given according to space group  $Pm\bar{c}n$  (a further alternative orientation of  $Pnma$ ) by which the structure is described most conveniently. The structure of orthorhombic  $\text{WO}_3$  is obtained from that of  $\text{MoO}_3$  formally by translating every second double layer by  $\pm a/2(\text{MoO}_3, Pbnm) = \pm c/2(Pmnb)$ . The resulting arrangement is one of almost c.c.p. of the O atoms. A certain extension along  $[010]$  ( $\text{MoO}_3$ ) is expressed by the above calculated difference of  $\sim 0.6 \text{ \AA}$ . In fact, the deviation is small as the ratio volume of the unit cell/number of O atoms shows: triclinic  $\text{WO}_3$  17.58, monoclinic  $\text{WO}_3$  17.62, orthorhombic  $\text{WO}_3$  17.75, tetragonal  $\text{WO}_3$  17.98  $\text{\AA}^3$ . The value for  $\text{MoO}_3$  is 16.9  $\text{\AA}^3$ .

The most general among the fourfold equipoints in this space group No. 62— $D_{2h}^{10}$  is 4(c). If this is occupied by the atoms of  $\text{WO}_3$ , the W atoms should have coordinates close to 000,  $0\frac{1}{2}0$ ,  $\frac{1}{2}0\frac{1}{2}$ ,  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  as can be concluded from Fig. 2. If

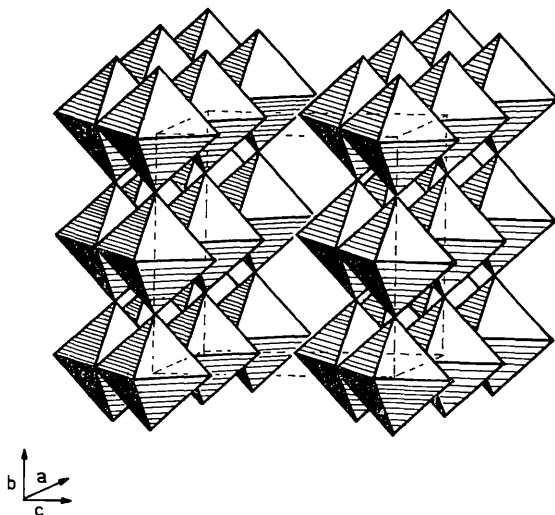


Fig. 2. The proposed structure of orthorhombic  $\text{WO}_3$  drawn as idealized octahedra. The crystal axes correspond to space group  $Pm\bar{c}n$ .

the W atoms do have these coordinates exactly [which represent equipoint 4(a)] greater differences in bond distances as compared with those in  $\text{MoO}_3$  must result. This is most likely so, as it is in accord with the differences in structural behaviour between Mo and W. How far pseudosymmetry in orthorhombic  $\text{WO}_3$  towards the space group  $Bbmm$  (standard  $Cmcm$ ; all atoms on  $mm$ ), found in  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$ , will be realized, can be seen only by the structure determination. The lattice parameters of this compound are given also in Table 1. The structure of orthorhombic  $\text{WO}_3$  already contains the arrangement of two kryptocells of tetragonal  $\text{WO}_3$  (Kehl, Hay & Wahl, 1952).

The true arrangement of the electric dipole chains in orthorhombic  $\text{WO}_3$  can of course be elucidated only by the structure determination, but by analogy with  $\text{MoO}_3$ , so far no reasons for internal repulsions can be seen.

To a certain degree, the arrangement of dipole chains in orthorhombic  $\text{WO}_3$  can be predicted by comparison with those in  $\text{WO}_2\text{Cl}_2$  (Jarchow, Schröder & Schulz, 1968).<sup>\*</sup> This structure also has W—O dipole chains in two directions, namely along  $[001]$  and  $[010]$  (space group  $B11b$ ). The first ones are antiparallel (two per unit cell) while the second are parallel by translation. Structural equivalence of lattice directions between  $\text{WO}_2\text{Cl}_2$  ( $A11a$ ) and  $\text{WO}_3$  ( $P2_1/n$ ) has been shown (Schröder, 1973) to exist in the following way  $[100] \triangle [010]$  and  $[010] \triangle [001]$ . If the setting  $B11b$  is used, corresponding directions in  $\text{WO}_2\text{Cl}_2$ ,  $\text{WO}_3$  ( $P2_1/n$ ) and  $\text{WO}_3$  ( $Pmnb$ ) are along equivalent lattice directions, neglecting the obliqueness of the  $\text{WO}_2\text{Cl}_2$  cell and, because of the centring of this cell, taking only half its corresponding lattice parameter. From comparison with  $\text{MoO}_3$  ( $Pmnb$ ) where we have dipoles along  $[010]$  and  $[001]$ , we may assume that in orthorhombic  $\text{WO}_3$  ( $Pmnb$ ) they are also along these directions.

<sup>\*</sup> In the paper of Jarchow, Schröder & Schulz (1968), the labelling of the atoms in Fig. 4 is incorrect. W(1) is linked to Cl(1), Cl(2), O(1), O(2) with the coordinates given in Table 2 [except those for Cl(1) and Cl(2)] and to two more symmetry-related O atoms, labelled O(3) and erroneously O(2) in Fig. 4. The coordinates of Table 2 refer to the given orthorhombic cell. The transformation matrix applies only to the z values of the Cl atoms. The equivalent positions for  $A1a1$  are:  $x, y, z$ ;  $\frac{1}{2} + x, \bar{y}, z$ ;  $x, \frac{1}{2} + y, \frac{1}{2} + z$ ;  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ;  $c = 14.41 \text{ \AA}$ .

Table 1. Lattice parameters ( $\text{\AA}$ ) and space groups for  $\text{WO}_3$ ,  $\text{WO}_2\text{Cl}_2$ ,  $\text{MoO}_3$  and  $\text{Mo}_4\text{O}_{10}(\text{OH})_2$

	a	b	c	Space group	Reference
$\text{WO}_3^*$	7.13	7.33	3.84		(i)
$\text{WO}_3 (> 350^\circ\text{C})$	7.28	7.45	3.81		(ii)
$\text{WO}_3^*$	7.339	7.545	3.857		(iii)
$\text{WO}_3^*$	7.336	7.560	3.872		(iv)
$\text{WO}_3^*$	7.356	7.583	3.878		(v)
$\text{WO}_3^*$	7.341 (4)	7.570 (4)	3.877 (2)	$Pmnb$	(vi)
	3.877	7.341	7.570	$Pm\bar{c}n$	
$\text{WO}_3(\text{RT})$	7.306 (1)	7.540 (1)	7.692 (1)	$P2_1/n$	(vii)
$\text{WO}_2\text{Cl}_2(\text{RT})$	7.68 (1)	3.89 (1)	14.41 (2)	$A1a1$	(viii)
	7.20†	7.68	3.89	$B11b$	
$\text{MoO}_3(\text{RT})$	3.6964 (6)	13.855 (3)	3.9628 (7)	$Pmnb$	(ix)
$\text{Mo}_4\text{O}_{10}(\text{OH})_2(\text{RT})$	3.734	14.082	3.888	$Bbmm$	(x)

References: (i) Ueda & Ichinokawa (1951), (ii) Wyart & Foex (1951), (iii) Rosen, Banks & Post (1956), (iv) Perri, Banks & Post (1957), (v) Ackermann & Sorrell (1970), (vi) Salje & Viswanathan (1975), (vii) Loopstra & Rietveld (1969), (viii) Jarchow, Schröder & Schulz (1968), (ix) Kihlberg (1963/64), (x) Wilhelmi (1969).

<sup>\*</sup> Lattice parameters were taken from diagrams for  $480^\circ\text{C}$ ; † the value is  $14.41/2 \text{ \AA}$ , the original lattice parameter of  $13.90 \text{ \AA}$  for the monoclinic cell is incorrect (cf. footnote on this page); RT: room temperature value.

Some comments on the papers S. (1974), S. & V. (1975) and S. (1975) are given in the Appendix.\*

*Note added in proof:* The most recently published results on the doubling of the  $c$  axis in monoclinic  $\text{WO}_3$  (Lefkowitz, Dowell & Shieldt, 1975) confirm the equivalence of the lattice directions in  $\text{WO}_2\text{Cl}_2$ , monoclinic  $\text{WO}_3$  and orthorhombic  $\text{WO}_3$  given here, as well as earlier results (Schröder & Felser, 1972).

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\* The Appendix has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31508 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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*Acta Cryst.* (1976). **A32**, 344

**The residual in the case of a mixture of centric and acentric reflexions.** By P. E. NIXON\*, *Laboratory of Molecular Biophysics, South Parks Road, Oxford OX1 3PS, England*

(Received 10 September 1975; accepted 22 September 1975)

The value of the residual for a randomly wrong structure when calculated from a mixture of centrosymmetrical and non-centrosymmetrical structure factors is close to the value obtained by interpolation between the centric and acentric cases of Wilson [*Acta Cryst.* (1950). **3**, 397–398].

Wilson (1950) pointed out that it was useful to know the likely value of the crystallographic residual for a randomly wrong structure, and he showed that this was  $2\sqrt{2}-2$  if the Wilson (1949) centric distribution function applies, and  $2-\sqrt{2}$  if his acentric distribution function applies. In non-centrosymmetrical space groups other than  $P1$ , one has both centrosymmetrical and non-centrosymmetrical structure factors, and usually calculates the residual without separation of the structure factors into two sets.

From equations (1) and (5) of Wilson's 1950 paper

$$R_{\text{random}} = \frac{2\langle F \rangle - 4\langle G(F) \rangle}{\langle F \rangle}$$

where

$$G(F) = \int_0^F F' P(F') dF'$$

If a proportion  $c$  of the structure factors belongs to the centric distribution, and  $(1-c)$  to the acentric,

$$R_{\text{random}} = \frac{2c\langle F \rangle_c + 2(1-c)\langle F \rangle_A - 4c\langle G \rangle_c - 4(1-c)\langle G \rangle_A}{c\langle F \rangle_c + (1-c)\langle F \rangle_A} \quad (1)$$

\* Present address: Department of Chemistry, University of Auckland, Auckland, New Zealand.

where the subscripts  $C$  and  $A$  refer to the centric and acentric distributions used to average  $F$  and  $G$ . Values of these averages are given by Wilson (1950): substitution in (1) gives

$$R_{\text{random}} = \frac{(4-2\sqrt{2})c + \pi(1-\sqrt{2}/2)(1-c)}{\sqrt{2}c + \frac{\pi}{2}(1-c)} \quad (2)$$

which reduces to Wilson's equations (8) and (10) when  $c=1$  and 0 respectively. A straight line interpolation between the limiting values is given by

$$R_{\text{random}} \approx 2-\sqrt{2} + (3\sqrt{2}-4)c \approx 0.59 + 0.24c \quad (3)$$

Use of (3) rather than the more exact (2) involves an error never greater than 0.006.

I am grateful to the Medical Research Council, London, for a scholarship in training in research methods.

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