JOURNAL OF SOLID STATE CHEMISTRY **29**, 429–434 (1979)

Structural Study of a New Hexagonal Form of Tungsten Trioxide

B. GERAND, G. NOWOGROCKI, J. GUENOT, AND M. FIGLARZ*

Départment de Chimie, Université de Picardie 33, rue Saint Leu, 80039 Amiens Cedex; Laboratoire de Chimie des Matériaux Divisés, Université de Paris 7, 2 Place Jussieu 75221 Paris Cedex 05, France

Received June 15, 1978; revision received November 30, 1978

A new form of tungsten trioxide WO_3 has been obtained by dehydration of $WO_3 \cdot 1/3\ H_2O$ hydrate. The structural study was carried out from X-ray powder diffraction and selected area electron diffraction data. The crystallographic characteristics are: the hexagonal system; $a = 7.298(2)$ Å, $c = 7.798(3)$ Å; $Z = 6$. This hexagonal WO_3 is built up of slightly distorted (WO_6) octahedra sharing their corners arranged in six-membered rings in layers normal to the hexagonal axis; stacking of such layers leads to formation of large hexagonal tunnels. Some confirmations of this structure were made by high-resolution electron microscopy. Powder X-ray diffraction allowed us to determine an average structure. Absence of suitable single crystals has not permitted us to perform a complete structural determination. Although the existence of such a hexagonal structure for pure WO_3 had been considered as likely, it had not been hitherto observed.

Introduction

Tungsten trioxide, WO_3, exists in several polymorphic forms. They are stable within well-defined temperature ranges and transform into each other reversibly. All these forms have structures of the ReO_3 type, i.e., can be described as constructed from (WO_6) octahedra linked by corner sharing, but they are less symmetrical than ReO_3 owing to distortions of the (WO_6) octahedra (*1*).

In the present paper, we report results of a structural study concerning a new form of tungsten trioxide which cannot be obtained from the known forms. The structure is also built from (WO_6) octahedra sharing their corners but their arrangement results in a hexagonal symmetry. We have not succeeded in preparing large enough single crystals, so the structural determination was carried out from X-ray powder diffraction and selected area electron diffraction data. These data allowed us to determine an average structure but absence of suitable single crystals has not permitted us to perform a complete structural determination. Some confirmation was obtained by high-resolution electron microscopy.

Preparation

Hexagonal tungsten trioxide is the product of total dehydration by dry heating of a hydrate, $WO_3 \cdot \frac{1}{3} H_2O$. This hydrate $WO_3 \cdot \frac{1}{3} H_2O$ was prepared by hydrothermal treatment at 120°C of an aqueous suspension of either tungstic acid gel or crystallized $WO_3 \cdot 2H_2O$.

For further discussion about chemical composition of hexagonal WO_3 we recall the preparations of the starting materials. The tungstic acid gel was prepared (*2*) by mixing solutions of sodium tungstate and

---

* Author to whom correspondence should be addressed.

0022-4596/79/090429-06$02.00/0

Printed in Great Britain

hydrochloric acid cooled at 5°C. The yellowish gel obtained was washed with distilled water and centrifugated; this washing process was repeated five times. To obtain the hydrate $WO_3 \cdot 2\ H_2O$, the washed gel was dispersed in distilled water and the solution was ripened at constant temperature (*2*).

A detailed account of the formation of $WO_3 \cdot \frac{1}{3} H_2O$, its analysis, and its structure will be published in another paper.

Hexagonal WO_3 was obtained by dehydration of $WO_3 \cdot \frac{1}{3} H_2O$ in a nitrogen–oxygen (80–20%) atmosphere by an isotherm treatment at 290°C or by a slow linear heating up to 420°C.

Due to the method of preparation the most probable impurity is sodium: Atomic absorption spectrophotometry within the limit of sensitivity of this method yielded information which allowed us to rule out any sodium impurity. Semiquantitative analysis by emission spectroscopy did not indicate the presence of alkaline, alkaline-earth, or transition metals in significant quantities (K, Ca $\simeq$ 100 ppm, others <50 ppm). Due to these results the formation of hexagonal tungsten bronzes (*3*), pseudohexagonal compounds such as $MoW_{3n-1}O_{9n}$ (*4*) or $K_xWO_{3+x/2}$ tungstate (*5*) can be discarded.

Unlike M_xWO_3 bronzes which are strongly colored, even for very low values of x, hexagonal WO_3 occurs as a white powder which can be slightly yellowish if containing traces of monoclinic WO_3.

Crystallographic Study

Crystallographic data have been collected with an X-ray powder diffractometer in reflection mode by the Θ–2Θ scanning technique using monochromatized cobalt $K\bar{\alpha}$ radiation. The scanning rate was 1° θ/20 min. The diffracted intensities were estimated by planimetry of peak recording and corrected for Lorentz polarization effects.

The powder diagram can be indexed in the hexagonal system (Table I). A least-squares refinement of the lattice parameters, using $\lambda K\bar{\alpha} = 1.79021$ Å, leads to $a = 7.298(2)$ Å, $c = 3.899(2)$ Å. As seen in Table I, there is no systematic absence of reflections, so eight space groups are possible. The specific mass

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR HEXAGONAL WO_3

$h\ k\ l^a$	$I_{exp}{}^b$	d_{obs}	d_{calc}
1 0 0	55	6.337	6.320
0 0 1	52	3.911	3.899
1 1 0	23	3.655	3.649
1 0 1	22	3.318	3.318
2 0 0	100	3.165	3.160
1 1 1	9	2.667	2.664
2 0 1	47	2.455	2.455
2 1 0	7	2.388	2.389
3 0 0	5	2.109	2.107
2 1 1	4	2.040	2.037
0 0 2	6	1.953	1.949
1 0 2	7	1.864	1.863
3 0 1		1.852	1.853
2 2 0	22	1.824	1.824
3 1 0	9	1.753	1.753
1 1 2	3	1.721	1.719
2 0 2	32	1.659	1.659
2 2 1		1.654	1.653
3 1 1	7	1.599	1.599
4 0 0	13	1.581	1.580
2 1 2	<1	1.511	1.510
4 0 1	10	1.464	1.464
3 2 0	<1	1.453	1.450
3 0 2	<1	1.430	1.431
4 1 0	3	1.376	1.379
3 2 1	<1	1.358	1.359
2 2 2	6	1.332	1.332
3 1 2	6	1.303	1.300
4 1 1		1.303	1.300
0 0 3		1.303	1.299
1 0 3	<1	1.274	1.273
4 0 2	4	1.228	1.227
1 1 3		1.228	1.224
3 3 0	<1	1.216	1.216
5 0 1	<1	1.200	1.202
2 0 3		1.200	1.202
4 2 0	<4	1.194	1.194

[a] For the true cell, l must be doubled.

[b] I_{exp} before Lorentz polarization correction.

of the compound was determined by hydrostatic method in CCl_4; the measured value, 6.36 g cm^{-3}, is in good agreement with the calculated value for three formula units WO_3 per cell, 6.43 g cm^{-3}.

The choice of the hexagonal cell has been confirmed by electron microdiffraction study. Hexagonal WO_3 particles present two types of habit depending on the starting reagent. Figure 1 shows the octagonal platelets characteristic of WO_3 proceeding from $WO_3 \cdot 2\,H_2O$; if the starting material is tungstic acid gel, WO_3 is obtained as needle aggregates (Fig. 2). Electron microdiffraction shows that these two types of particles lie on the (100) and (001) planes, respectively (Figs. 3 and 4). Octagonal particles are well fitted for a study with an eucentric goniometer stage. By tilting about the [001] axis, several planes of the reciprocal lattice could be explored (Fig. 5). These selected area electron diffraction patterns show good agreement for parameter a, but superreflections appear, indicating that the c parameter must be doubled. These weak spots are present in all reciprocal sections containing c^* (Figs. 3 and 5).

The true cell parameters are then: $a = 7.298(2)$ Å, $c = 7.798(3)$ Å, and $Z = 6$.

The streaks which are observable essentially along c^* indicate stacking faults along c and possible disorder within the set of (001) planes.

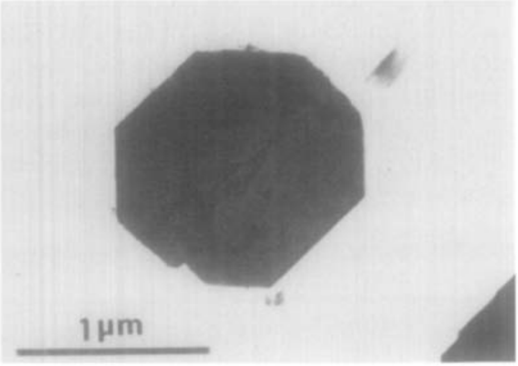

FIG. 1. Thin crystals of hexagonal WO_3 obtained from the dihydrate (octagonal platelets); particles lying on the (100) plane.

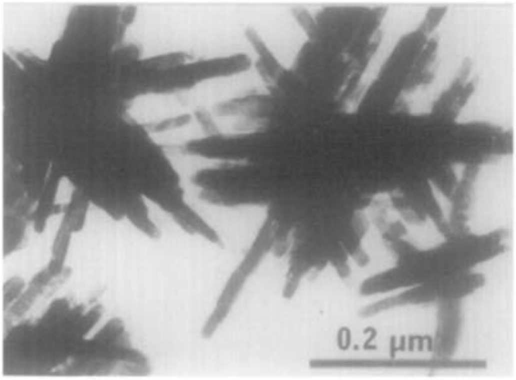

FIG. 2. Thin crystals of hexagonal WO_3 obtained from a tungstic acid gel (needle aggregates); particles lying on the (001) plane.

In addition, it is to be noted that from the electron microscopy study, we can forsee difficulties in X-ray diffraction intensity measurement owing to orientation caused by the pronounced anisotropy of particle habit. (In order to diminish this preferred orientation the samples have been ground.)

Crystal Structure

A too-small number of reflections are available (only 21 intensities are measurable with accuracy) for the structure to be determined ab initio from the X-ray powder data. Fortunately, the diffraction pattern presents

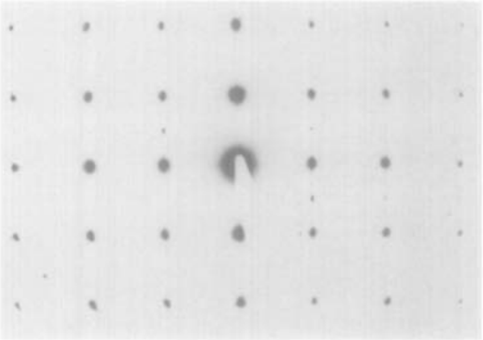

FIG. 3. Electron microdiffraction taken from a particle shown in Fig. 1; the (210)* reciprocal section.

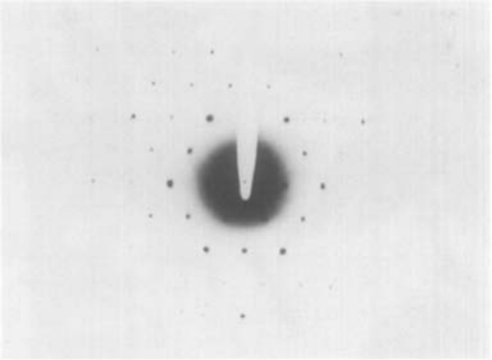

FIG. 4. Electron microdiffraction taken from a particle shown in Fig. 2; the (001)* reciprocal section.

some analogies with that of hexagonal tungsten bronzes. So, we shall use as a likely model the crystal structure of the latter as it has been published by Magneli (*3*). This structure was described in the space group $P6_3/mcm$ with cell parameters $a \simeq 7.4$ Å, $c \simeq 7.6$ Å.

The attempts at the resolution of the structure have been performed with a least-squares refinement program adapted for powder data. Atomic scattering factors for tungsten and oxygen are those given by Cromer and Waber (*6*) and Tokonami (*7*). Preferred orientation correction has been applied by dividing all the $hk0$ intensities by a normalizing factor.

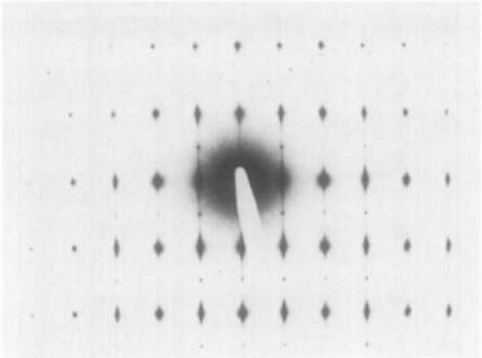

FIG. 5. Electron microdiffraction of hexagonal WO_3 taken from a crystal shown in Fig. 1. The crystal has been tilted around the [001] direction, angle of tilt 30°; the (110)* reciprocal section.

Absence in our X-ray data of reflection with odd values of l cannot give any precision on determination of parameters of the atomic positions.

This has led us to determine an average structure in the most symmetrical space group possible, $P6/mmm$, with the half-cell found by X-ray diffraction. The atomic positions are listed in Table II; their refinement will give a first approximation of the true structure. R_1 factor decreases rapidly to 0.114 in the hypothesis of isotropic thermal vibration for all atoms. Introduction of anisotropic thermal parameters for tungsten leads to $R_1 = 0.098$, $R_2 = 0.109$, and to the final atomic parameters of Table III.

Table IV shows good agreement between observed and calculated intensities.

Of course there remain rather important imprecisions due to the small number of observed intensities but the structural model is supported by the X-ray analysis and the average structure can be considered a good approximation of the true structure. It is not possible to go further in the determination of the real structure without data collected on a single crystal.

Description of the Structure

Tungsten atoms are bonded to six oxygen atoms in a near-perfect octahedral coordination as shown by the calculated interatomic distances of Table V. Each oxygen atom is shared by two octahedra. These octahedra are arranged in layers normal to the hexagonal axis; they form six-membered rings in (001) plane (Fig. 6). In the complete

TABLE II

ATOMIC POSITIONS IN HEXAGONAL WO_3 HALF-CELL[a]

3 W	$\frac{1}{2}\,0\,0$;	$0\,\frac{1}{2}\,0$;	$\frac{1}{2}\,\frac{1}{2}\,0$
3 O_1	$\frac{1}{2}\,0\,\frac{1}{2}$;	$0\,\frac{1}{2}\,\frac{1}{2}$;	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$
6 O_2	$x\;2x\;0$;	$2\bar{x}\;\bar{x}\;0$;	$x\;\bar{x}\;0$;
	$\bar{x}\;2\bar{x}\;0$;	$2x\;x\;0$;	$\bar{x}\;x\;0$

[a] Space group $P6/mmm$ ($Z = 3$).

TABLE III

FINAL ATOMIC AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (AVERAGE STRUCTURE IN WO$_3$ HALF-CELL)

Atom	x	y	z	β_{iso} (Å^2)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	$\frac{1}{2}$	0	0	2.6	0.015(4)	0.013(6)	0.057(9)	$\frac{1}{2}\beta_{22}$	0	0
O$_1$	$\frac{1}{2}$	0	$\frac{1}{2}$	6.3(3.5)						
O$_2$	0.212(6)	0.424	0	5.2(3.3)						

structure, stacking of such layers along the hexagonal axis leads to formation of large hexagonal tunnels with very high occupancy possibilities: The distance of crystallographic position $(0, 0, \frac{1}{2})$ to O$_2$ atoms being 3.32 Å, even large molecules or ions can be accommodated. The narrowest parts of the tunnels still have large dimensions: The distance of (0, 0, 0) position to O$_2$ is 2.68 Å.

If the presence of metallic ions in the hexagonal tunnels can be rejected on analytical grounds, the occupancy by water molecules can be considered. This hypothesis, compatible with the tunnel dimensions, does not, however, improve R_1 and R_2 factors: The occupancy factor of the crystallographic position takes a rather high value (0.17) but with a very large standard deviation (0.45). Therefore, presence of water cannot be ascertained from powder data only. Infrared absorption spectroscopy and differential thermal analysis indicate the presence of only a little adsorbed water.

This crystal structure has been confirmed by high-resolution electron microscopy (*8*). It is well known (*9*) that under certain experimental conditions (thin enough and well-oriented crystals, imaging conditions of the microscope, etc.), the image contrast in high-resolution electron microscopy can be considered as a projection on a plane perpendicular to the incident electron beam

TABLE IV

COMPARISON BETWEEN OBSERVED AND CALCULATED INTENSITIES[a]

$h\,k\,l$[b]	Multiplicity	I_{obs}	I_{calc}
1 0 0	6	9.00	13.72
0 0 1	2	33.66	30.10
1 1 0	6	12.05	11.45
1 0 1	12	19.87	14.78
2 0 0	6	70.35	72.62
1 1 1	12	13.17	12.98
2 0 1	12	83.11	82.50
2 1 0	12	9.2	8.01
3 0 0	6	8.22	9.56
2 1 1	24	11.12	9.34
0 0 2	2	19.05	21.01
1 0 2 3 0 1	12 12	25.17	23.32
2 2 0	6	53.91	53.89
3 1 0	12	25.26	13.96[c]
1 1 2	12	10.96	9.76
2 0 2 2 2 1	12 12	138.17	138.67
3 1 1	24	32.61	18.76[c]
4 0 0	6	44.78	42.74
4 0 1	12	57.06	58.61
4 1 0	12	12.05	6.85
2 2 2	12	40.40	50.78[c]

[a] The $hk0$ experimental intensities are divided by 1.44.

[b] *l values for half-cell*

[c] Reflections rejected for final refinement ($R_1 = 0.057$, $R_2 = 0.052$ without these).

TABLE V

INTERATOMIC DISTANCES[a]

WO$_1$ = 1.95 Å
WO$_2$ = 1.89 Å
O$_1$O$_2$ = 2.72 Å
O$_2$O$_2'$ = 2.66 Å
O$_2$O$_2''$ = 2.68 Å

[a] The estimated standard deviations are about 0.02 Å.

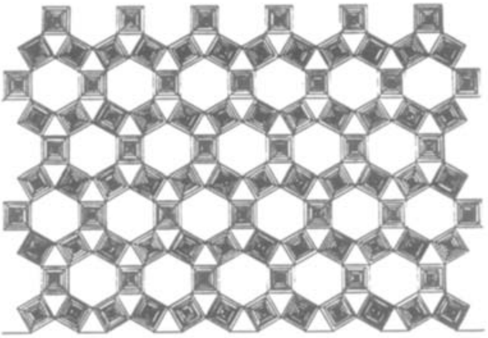

FIG. 6. Schematic view showing the main features of the hexagonal WO_3 structure; projection along the [001] axis. The (WO_6) octahedra are shaded.

of a function characteristic of the structure (electrostatic potentials or charge density distributions). The needle-like particles of hexagonal WO_3 (Fig. 2) are particularly well fitted for such a study: They are very thin crystals lying on (001) plane (Fig. 4), i.e., in a good orientation for imaging the essential structural features. Figure 7 presents such a high-resolution image. The contrast distribution is in fairly good agreement with the structural scheme of Fig. 6: Dark regions in the image represent the metal atom position in the crystal (*9*) and the hexagonal tunnels appear as large white regions. The values of the parameters measured by electron microscopy are also in good agreement with those calculated by X-ray diffraction.

Conclusion

We have prepared a new form of tungsten trioxide WO_3 and established its hexagonal structure by means of X-ray powder diffraction, electron microdiffraction, and high-resolution electron microscopy.

This hexagonal WO_3 can only be obtained from the hydrate $WO_3 \cdot \frac{1}{3} H_2O$.

We have shown that impurities are not responsible for the structure stability of this hexagonal form; as will be shown in the near future, the structure of this oxide is closely related to that of the hydrate $WO_3 \cdot \frac{1}{3} H_2O$.

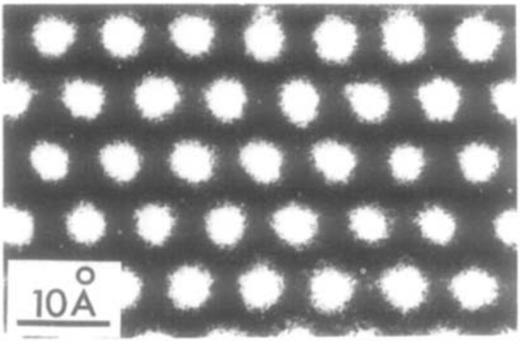

FIG. 7. High-resolution electron microscopy image of a thin portion of a crystal of hexagonal WO_3 lying on the (001) plane (see Fig. 2). The contrast distribution is in good accordance with the ideal structure projected on the (001) plane (Fig. 6).

The existence of this hexagonal form of WO_3 was considered likely by some authors (*4, 10*) but, so far, its preparation had not been achieved.

References

1. A. F. WELLS, "Structural Inorganic Chemistry," 4th ed., p. 474, Oxford Univ. Press (Clarendon), London/New York (1975).
2. K. FURUSAWA AND S. HACHISU, *Sci. Light* (*Tokyo*) **15**, 115 (1966).
3. A. MAGNELI, *Acta Chem. Scand.* **7**, 315 (1953).
4. J. GRAHAM AND A. D. WADSLEY, *Acta Crystallogr.* **14**, 379 (1961).
5. A. DESCHANVRES, G. DESGARDIN, B. RAVEAU, AND J. C. THOMAZEAU, *Bull. Soc. Chim. Fr.* **12**, 4537 (1967); P. GOODMAN, *Acta Crystallogr. Sect. B* **32**, 3280 (1976).
6. D. T. CROMER AND J. T. WABER, *Acta Crystallogr.* **18**, 104 (1965).
7. M. TOKONAMI, *Acta Crystallogr.* **19**, 486 (1965).
8. B. GERAND AND M. FIGLARZ, *in* "9th International Congress on Electron Microscopy" (J. M. Sturgess, Ed.), Vol. 1, p. 260, Toronto (1978).
9. J. M. COWLEY AND S. IIJIMA, *Z. Naturforsch. A* **27**, 445 (1972).
10. P. HAGENMULLER, *in* "Progress in Solid State Chemistry" (H. Reiss, Ed.), Vol. 4, p. 84, Pergamon, Elmsford, N.Y. (1971).