JOURNAL OF SOLID STATE CHEMISTRY 38, 312–320 (1981)

A New Tungsten Trioxide Hydrate, $WO_3 \cdot \frac{1}{3}H_2O$: Preparation, Characterization, and Crystallographic Study

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Received October 31, 1980; in revised form December 17, 1980

A new hydrate of tungsten trioxide, $WO_3 \cdot \frac{1}{3}H_2O$ has been obtained by hydrothermal treatment at 120°C of an aqueous suspension of either tungstic acid gel or crystallized dihydrate. This hydrate has been characterized by different methods. A crystallographic study was carried out from X-ray powder diffraction. The hydrate crystallizes in the orthorhombic system: a = 7.359(3) Å, b = 12.513(6) Å, c = 7.704(5) Å, Z = 12. The existence of structural relationships between the hydrate, $WO_3 \cdot \frac{1}{3}H_2O$, and the product of dehydration, hexagonal WO_3, has permitted us to propose a structural model in agreement with the experimental data. $WO_3 \cdot \frac{1}{3}H_2O$ must be regarded as an interesting compound because its dehydration leads to a new anhydrous tungsten trioxide, hexagonal WO_3.

Introduction

"Tungstic acids" or tungsten trioxide hydrates are the terms applied to various solids precipitated by strong acids from a sodium tungstate solution; different phases may occur, depending on the precipitation conditions.

Although the tungstic acids system has been extensively investigated for a long time and these compounds have often been mentioned in earlier literature (*1*) as well as in more recent years (*2–4*), the existence of some compounds remains confused. Among these hydrates the existence and structure of tungsten trioxide mono- and dihydrate are well established (*4–6*) by comparison with $MoO_3 \cdot H_2O$ and $MoO_3 \cdot 2H_2O$. Among the other compounds, a hemihydrate, $WO_3 \cdot \frac{1}{2}H_2O$, has been claimed to exist by several authors (*7–9*); substitution of cations or large variations in composition has been reported (*4*) for a phase-C-related to the hemihydrate. Morley (*7*) thought this phase C was a hemihydrate. Freedman *et al.* (*4*) have identified this phase C by chemical analysis and X-ray powder diffraction, and concluded that it was a sodium octotungstate with large variation in composition, $Na_2O(WO_3 \cdot \frac{1}{2}H_2O)_n$, where n can vary from 10 to 40. The X-ray diffraction patterns for various phase C's showed some shifts in line spacing with variation in composition. Biehler (*9*) has prepared a tungsten trioxide hemihydrate by different methods. He characterized the hydrate only on chemical analysis and thermogravimetry, and he found a sodium content less than 1%.

Some authors have identified the phase C and the hemihydrate by their X-ray powder diffraction patterns, but structural data are completely missing.

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0022-4596/81/090312-09$02.00/0

It may be concluded from this rapid survey of the literature that the existence of the hemihydrate is still uncertain. In the course of a study on the reactivity of tungsten trioxide hydrates we have obtained a new tungsten trioxide hydrate which was characterized as $WO_3 \cdot \frac{1}{3}H_2O$; this hydrate presents some similarities with the phase C and the hemihydrate previously discussed. We have studied this $WO_3 \cdot \frac{1}{3}H_2O$ phase in some detail and present here the results obtained in this work.

Preparation

$WO_3 \cdot \frac{1}{3}H_2O$ was prepared by hydrothermal treatment at 120°C of an aqueous suspension of either tungstic acid gel or well crystallized $WO_3 \cdot 2H_2O$.

(a) The tungstic acid gel was prepared according to Zocher's method (*10*) by mixing solutions of sodium tungstate (7 g in 100 cm^3 of permuted water) and hydrochloric acid (50 cm^3 of a normal solution) cooled at 5°C. The yellowish gel obtained after leaving the mixture for about 2 hours was washed with 400 cm^3 of water by stirring; after centrifugation the supernatant liquid was removed and this washing–centrifugation process was repeated five times. The gel was then dispersed in 500 cm^3 of water and the suspension thus obtained was heated for about 20 hours in an autoclave (Autoclave Engineers) at 120°C. During the isothermal reaction the slurry was continually stirred. The autoclave operated in a nitrogen (80%)–oxygen (20%) atmosphere, the pressure before heating was 10 bars.

(b) The second method of preparation started with the dihydrate $WO_3 \cdot 2H_2O$ prepared according to Furusawa (*11*). The washed tungstic acid gel was dispersed in 4000 cm^3 of water and the turbid solution obtained was ripened for 1 or 2 weeks at constant temperature (in the range 5–25°C). After a week, highly monodispersed microcrystals of dihydrate were obtained. These are thin perfectly regular-shaped rectangular platelets about 2 μm in length, 0.5 μm in width and with a thickness of several hundred angstroms (100–1000 Å, depending on the ripening temperature). Three grams of $WO_3 \cdot 2H_2O$ was dispersed in 500 cm^3 of water and this slurry was treated at 120°C in the autoclave for a few days.

These two methods of preparation lead to a white powder which was characterized by an identical X-ray diffraction pattern (Table I).

It was observed that the white phase is obtained pure only below a temperature threshold, which was 120°C; above this temperature, the product was yellowish and other phases were detected as $WO_3 \cdot 1H_2O$ and monoclinic WO_3. Below 120°C, the rate of reaction becomes too slow.

Different attempts to vary the methods of preparation with other starting materials (for example the di- or monohydrate obtained by the method of Freedman (*3*)) were unsuccessful, leading always to a mixture of the white phase, monohydrate, and monoclinic WO_3. We have not succeeded in preparing large enough single crystals to carry out a complete structural determination and our crystallographic study was limited to the data obtained from X-ray powder diffraction.

Characterization

The characterization was done using electron microscopy, electron diffraction, X-ray powder diffraction, infrared spectrometry, and thermal analysis (TGA, DTA); the samples were analyzed by atomic absorption spectrometry and emission spectroscopy.

This white phase has been identified as a tungsten trioxide hydrate $WO_3 \cdot \frac{1}{3}H_2O$: the product of dehydration is anhydrous WO_3 and the H_2O content was determined as the loss in weight on heating.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $WO_3 \cdot \frac{1}{3}H_2O$

hkl	I_{exp}	d_{obs}	d_{calc}
020[a]	19	6.268	6.256
111[a]	36	4.899	4.897
002[a]	42	3.848	3.852
200[a]	7	3.679	3.679
131	26	3.281	3.282
022			3.280
220[a]	100	3.172	3.172
040[a]		3.131	3.128
202[a]	7	2.658	2.661
222[a]	40	2.449	2.448
042[a]		2.432	2.428
240	8	2.379	2.383
113			2.380
311[a]	4	2.298	2.298
151[a]		2.263	2.265
133	4	2.095	2.096
060			2.086
331[a]	7	2.038	2.039
242[a]		2.028	2.027
004[a]	5	1.926	1.926
024			1.841
400	14	1.840	1.840
062			1.834
260[a]	14	1.813	1.814
420[a]	4	1.765	1.765
313[a]		1.757	1.756
351		1.708	1.708
204	9		1.706
171		1.697	1.696
402		1.660	1.660
224	28		1.646
262		1.643	1.641
044			1.640
333		1.635	1.632
422[a]	3	1.605	1.605
440[a]	9	1.586	1.586
080[a]	4	1.564	1.564

[a] Reflections used in refinement of cell parameters.

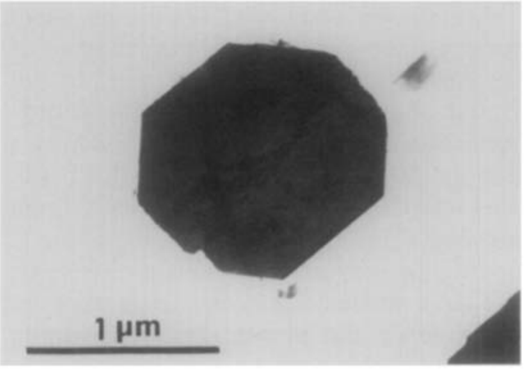

FIG. 1. Thin octagonal platelets of $WO_3 \cdot \frac{1}{3}H_2O$ obtained from the dihydrate.

According to the method of preparation, two kinds of microcrystals were obtained. Figure 1 shows the octagonal platelets of $WO_3 \cdot \frac{1}{3}H_2O$ proceeding from the dihydrate; these platelets have a mean size of about 1 μm, their thickness is between 1000 and 2000 Å. The electron microdiffraction of an isolated particle indicates that the particles are lying on the (100) plane; streaks show planar defects along the [001] axis; twins in the microcrystals are present. If the starting material is tungstic acid gel, $WO_3 \cdot \frac{1}{3}H_2O$ is obtained as needle aggregates twinned at 60° (Fig. 2); the needles are lying on the (001) plane. Their length is about 2000 Å, with a width and thickness of about 200 Å. The two kinds of habitus thus obtained are determined by the growth mechanism.

$WO_3 \cdot \frac{1}{3}H_2O$ is stable until about 250°C, as shown by an X-ray powder diffraction study with a Guinier-Lenne heating camera (Fig. 3); above this temperature dehydration takes place, leading to a new anhydrous tungsten trioxide: hexagonal WO_3 (*12*).

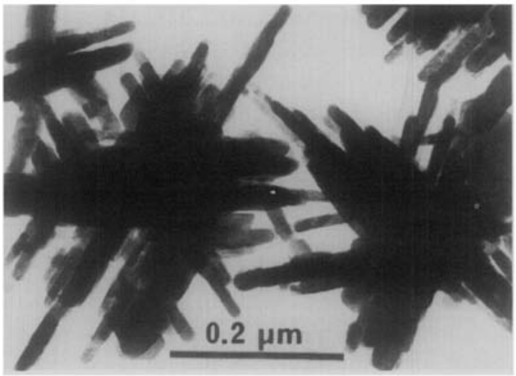

FIG. 2. Needle aggregates of $WO_3 \cdot \frac{1}{3}H_2O$ obtained from tungstic acid gel.

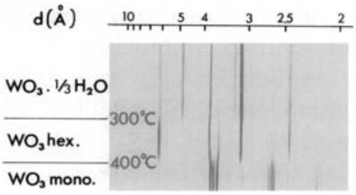

FIG. 3. X-Ray powder diffraction pattern of $WO_3 \cdot \frac{1}{3}H_2O$ on heating (Guinier-Lenne camera) showing the dehydration into hexagonal WO_3.

It was found by thermogravimetric analysis coupled with X-ray powder diffraction that the dehydration takes place in two steps. The first step corresponds to the evolution of adsorbed water without any structural change until 250°C. An NMR study, which will be published later, has shown the presence of OH groups bonded to the surface in addition to the adsorbed molecular water; these rather strongly bonded OH groups are certainly responsible for the relative difficulty of desorption. The second step (250–350°C) corresponds to the loss of structural water. These two steps are not clearly separated and it is therefore difficult to isolate $WO_3 \cdot \frac{1}{3}H_2O$ without adsorbed water. A typical TGA curve is given in Fig. 4, which illustrates the difficulty in separating these two steps by an appropriate heating procedure. It was found that the white hydrate retains up to 2% of adsorbed water (which is an amount similar to that of the structural water) depending on the kind of particles and their manner of conservation. This may be correlated to the specific surface area of the samples which are 22.6 and 3.5 $m^2 \cdot g^{-1}$ respectively for the needle aggregates and the octagonal platelets. The weight loss during the dehydration step corresponds to about $\frac{1}{3}H_2O$ per mole of WO_3; we sometimes found higher values, probably due to the incomplete evolution of adsorbed water and hydroxyl groups, but they were always less than 0.5 H_2O. We can therefore conclude that the formula of the hydrate is probably $WO_3 \cdot \frac{1}{3}H_2O$; this will be confirmed by the proposed structure in the crystallographic study.

The TGA was corroborated by differential thermal analysis: we observed an important baseline shift (due to evolution of adsorbed water) followed by an endotherm at about 350°C (dehydration of $WO_3 \cdot \frac{1}{3}H_2O$).

From the infrared spectra (Fig. 5) it can be confirmed that $WO_3 \cdot \frac{1}{3}H_2O$ retains a great amount of adsorbed water: weak and broad band at 1630 cm^{-1} and very broad band in the 3500 cm^{-1} region. The first band may be assigned to the bending vibration,

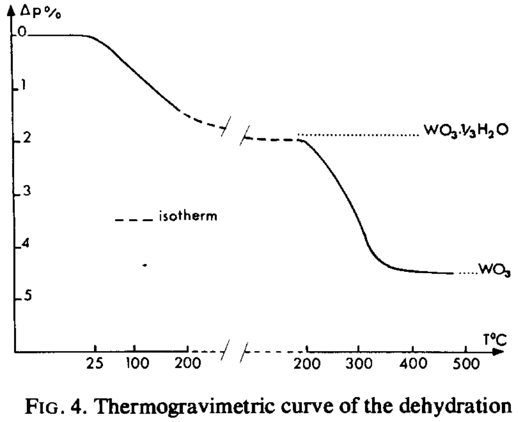

FIG. 4. Thermogravimetric curve of the dehydration of $WO_3 \cdot \frac{1}{3}H_2O$ showing the evolution of adsorbed water and the dehydration of the hydrate.

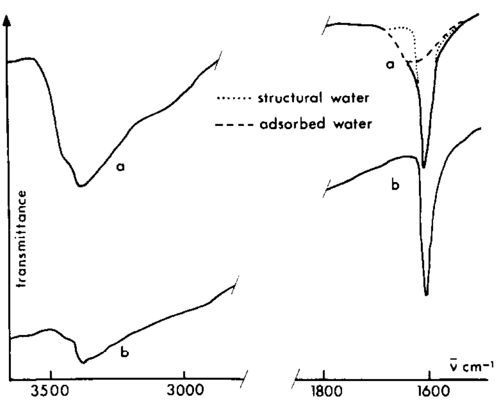

FIG. 5. Infrared spectra of $WO_3 \cdot \frac{1}{3}H_2O$: (a) needle aggregates; (b) octagonal platelets.

δ_{H_2O}, of adsorbed water molecules and the second mainly to the stretching vibration, ν_{OH}, of adsorbed water molecules hydrogen bonded to the OH adsorbed groups. As previously indicated, the needle aggregates adsorbed much more water (Fig. 5a) than the octogonal platelets (Fig. 5b). Concerning the structural water, ir spectrometry leads to interesting conclusions. A priori this structural water can be coordinated as OH hydroxyl groups or as water molecules. The existence of an intense and narrow band at 1605 cm^{-1} indicates that structural water is coordinated as water molecules; indeed this band cannot be assigned to adsorbed water (too strongly bonded molecules and too narrow band). The ν_{OH} vibration associated with this structural water makes a contribution to the broad band at 3500 cm^{-1}, but is hidden by the adsorbed water and OH groups. If structural water were coordinated as hydroxyl groups we would expect only ν_{OH}, so the existence of an intense and narrow band at 1605 cm^{-1} proves unambiguously that structural water is coordinated as H_2O molecules. This is confirmed by the NMR study.

The characterization was completed by the analysis of the samples. Due to the methods of preparation, the most probable impurity is sodium. Atomic absorption spectrometry, within the limit of sensitivity of this method, yielded information which allowed us to rule out any sodium impurity. For comparison, we analysed Freedman's phase C: a sodium content of 0.86% was found compared with the value of 0.62% obtained by Freedman (*4*). Semiquantitative analysis by emission spectroscopy did not indicate the presence of alkaline, alkaline-earth, or transition metals in significant quantities (*12*).

This leads us to conclude that our white phase cannot be considered as the phase C octotungstate of Freedman (*4*) and must be considered as a hydrate $WO_3 \cdot \frac{1}{3}H_2O$. There is probably a relation between these two phases, one deriving from the other by substitution of the water molecules' hydrogen by sodium leading to the ranges of phase homogeneity $Na_2O(WO_3 \cdot \frac{1}{2}H_2O)_{8-40}$; the excess of water with regard to $\frac{1}{3}H_2O$ being due to adsorbed water. Concerning the Biehler phase $WO_3 \cdot \frac{1}{2}H_2O$, we consider this compound as an impure (containing some sodium) $WO_3 \cdot \frac{1}{3}H_2O$ phase of poor crystallinity (as can be seen from the X-ray powder diffraction pattern); the discrepancy concerning the water content must be related to the water adsorption surface phenomenon, whose importance we have already indicated.

Crystallographic Study

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

The evolution of the diffraction pattern during heating of $WO_3 \cdot \frac{1}{3}H_2O$ (Fig. 3) strongly suggests a close relationship between the parameters of the hydrate and anhydrous tungsten trioxide. An indexation was tested in an orthorhombic cell derived from hexagonal WO_3 (*12*) and it showed reasonable agreement: refinement of parameters was performed using only the 20 unambiguously indexed reflections and led to values: $a = 7.359(3)$ Å, $b = 12.513(6)$ Å, $c = 7.704(5)$ Å. Table I lists all the observed reflections up to $\theta < 35°$, the given intensities being the rounded values before Lorentz and polarization corrections. For some reflections, the maxima are sufficiently separated to determine the Bragg angles, but too close to evaluate the individual intensities.

The conditions *h*, *k*, *l*, all even or all odd are quite obvious and clearly point to a face-centered cell; existence of reflections such as 200, 020 and 022 forbids the presence of a *d* glide plane, so the only space groups to consider are *F*222, *Fmm*2 or *Fmmm*.

The specific mass of the compound was determined by hydrostatic method in CCl_4; the measured value, 6.35 $g \cdot cm^{-3}$, is in good agreement with the calculated value for 12 formula units per cell, 6.68 $g \cdot cm^{-3}$.

Crystal Structure

A far too small number of reflections can be measured with any accuracy: only 20 intensities are available for the structural determination. Furthermore, 10 of these are superpositions of two or more reflections and the pronounced anisotropy of particle habitus causes a preferred-orientation effect. It is quite evident that we can, at best, make an educated guess and verify that it does not conflict with the experimental results.

A study by electron microscopy and electron microdiffraction of the dehydration of $WO_3 \cdot \frac{1}{3}H_2O$ indicates that the parent ($WO_3 \cdot \frac{1}{3}H_2O$) and product (hexagonal WO_3) phases are pseudomorphous and related by definite and constant orientation relationships:

$$(100)\ WO_3 \cdot \tfrac{1}{3}H_2O \parallel (100)\ \text{hex.}\ WO_3,$$

$$[001]\ WO_3 \cdot \tfrac{1}{3}H_2O \parallel [001]\ \text{hex.}\ WO_3.$$

A comparison of the unit cells of hexagonal WO_3 (*12*) ($a = 7.298$ Å, $c = 7.798$ Å) and of $WO_3 \cdot \frac{1}{3}H_2O$ shows that the two cells are closely related: $a_{\text{hydrate}} \cong a_{\text{hex.WO}_3}$, $b_{\text{hydrate}} \cong 3b_{\text{hex.WO}_3}$, $c_{\text{hydrate}} \cong c_{\text{hex.WO}_3}$.

So to get an idea of the unknown crystal structure of $WO_3 \cdot \frac{1}{3}H_2O$, we shall start with the assumption that the atomic arrangement in the (001) plane is the same in the parent and product structures. However, the orthorhombic cell of the hydrate being face centered, it cannot be a simple distortion of the hexagonal cell of WO_3. The lattice points at $\frac{1}{2}, 0, \frac{1}{2}$ and $0, \frac{1}{2}, \frac{1}{2}$ can only be obtained by a translation of $a/2$ of half of the layers perpendicular to *c*. Based on these arguments, a structural model may be proposed for $WO_3 \cdot \frac{1}{3}H_2O$ as represented in Fig. 6.

The atomic positions are then quite compatible with the three possible space groups.

Some attempts at structure resolution were performed with a least-squares refinement program adapted for powder data, which takes into account multiplicity, superposition of reflections, and preferred-orientation correction for the *hk*0 layer (we used the X-ray powder data obtained from the needle aggregates).

As we have seen from the infrared study, structural water is coordinated as H_2O mol-

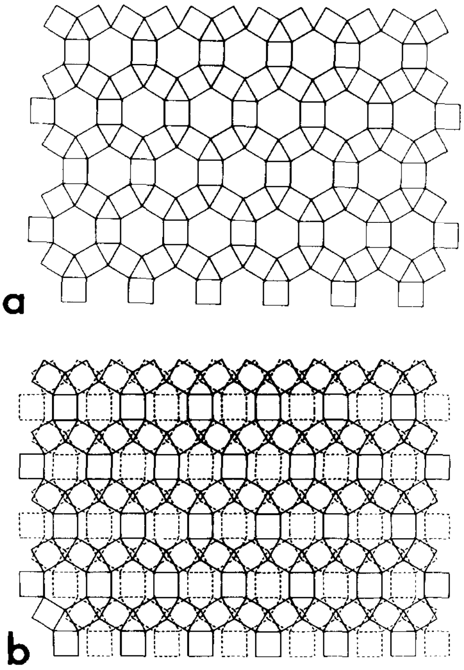

FIG. 6. The structural filiation between the product and parent phases in the dehydration of $WO_3 \cdot \frac{1}{3}H_2O$: (a) schematic crystal structure of hexagonal WO_3 projected along the *c* axis; (b) schematic crystal structure of orthorhombic $WO_3 \cdot \frac{1}{3}H_2O$ projected along the *c* axis.

ecules and we have found 12 formula units per cell. This implies that the four water molecules in the cell must be located in a fourfold crystallographic position directly linked to tungsten atoms. Therefore the only possible space group is *Fmm*2. Due to the large number of refinable parameters, the refinement was very sensitive to the starting set of values. After some trials, it was possible to find physically acceptable atomic coordinates which led to final *R* values: $R_1 = 0.057$, $R_2 = 0.052$ for 20 intensities. The refined parameters were scale factor, eight atomic coordinates, and two temperature factors for tungsten atoms; *z* of W(1) atom was fixed at 0 to set the origin, *z* of oxygen atom O(3) and temperature factors of oxygen were held constant during refinement.

The final parameters are listed in Table II; the large standard deviations are obviously due to the insufficient number of data.

It is evident that the values obtained are of low accuracy, but even such a limited agreement between observed and calculated intensities (Table III) indicates that the structural hypothesis is basically correct and that these results can be considered as a good approximation of the true structure. It is not possible to go further in the structural determination without intensities collected on a single crystal.

TABLE II

ATOMIC POSITIONAL COORDINATES AND THERMAL PARAMETERS IN $WO_3 \cdot \frac{1}{3}H_2O$[a]

Atom	*x*	*y*	*z*	*B*
W(1)	$\frac{1}{4}$	$\frac{1}{4}$	0	2.3(0.6)
W(2)	0	0	−0.06(4)	1.3(1.0)
O(1)	0	0.29(2)	0.04(5)	6.0
O(2)	0.17(2)	0.11(2)	0.01(4)	6.0
O(3)	$\frac{1}{4}$	$\frac{1}{4}$	0.25	6.0
O(4)	0	0	0.21(6)	6.0
O(5)	0	0	0.70(5)	6.0

[a] Standard deviations are given in parentheses.

TABLE III

OBSERVED AND CALCULATED[a] INTENSITIES FOR $WO_3 \cdot \frac{1}{3}H_2O$

hkl	Multiplicity	I_{obs}	I_{calc}
020	2	4.60	4.96
111	8	14.24	13.79
002	2	27.95	24.90
200	2	5.04	3.78
131	8	23.97	22.05
022	4		
220	4	101.75	103.22
040	2		
202	4	10.14	8.39
222	8	71.00	71.03
042	4		
240	4	14.45	13.79
113	8		
311	8	8.52	9.69
151	8		
133	8	9.53	11.04
060	2		
331	8	19.62	21.41
242	8		
004	2	16.81	13.49
400	2	49.12	50.67
024	4		
062	4		
260	4	49.30	50.20
420	4	14.75	11.07
313	8		
351	8	35.94	32.63
204	4		
171	8		
422	8	12.97	11.23
440	4	40.86	40.91
080	2	18.38	19.83

[a] The calculated intensities for *hk*0 reflections are multiplied by 1.35 to take into account preferred orientation.

Description of the Structure

The basic structural element is an infinite plane of (WO_6) octahedra sharing their corners and forming six-membered rings: these structural elements are similar to those found in hexagonal WO_3 (Fig. 6a). The complete structure can be described as a stacking of such layers along the [001] axis, one out of two layers being shifted by *a*/2 (Fig. 6b).

Table IV gives the interatomic distances W–O. All the tungsten atoms are bonded to six oxygen atoms in a slightly distorted octahedral coordination (Fig. 7). As for the final parameters listed in Table II, the estimated standard deviations are evidently quite large. W(1) is bonded to two O(1) atoms, two O(2) atoms, and two O(3) atoms. W(1) octahedron shares O(1) and O(2) atoms with neighboring octahedra in the same layer and its O(3) atoms with W(1) octahedra of adjacent layers above and below; this ensures the bonding between the layers and thus the stability of $WO_3 \cdot \frac{1}{3}H_2O$. W(2) is bonded to four O(2) atoms and to O(4) and O(5) atoms. If the O(2) atoms are shared by neighboring W(1) octahedra, the O(4) and O(5) atoms are only coordinated to W(2). As the W(2) atom is slightly below the plane of O(2), the deformation of W(2) octahedra is obviously caused by the difference in nature of bonding; the rather long W(2)–O(4) distance (2.1 Å) indicates that O(4) is probably the water molecule. Conversely the rather short distance W(2)–O(5) = 1.8 Å and the large angle O(5)–W(2)–O(2) ≃ 106° can be attributed to a double-bond character in W(2)–O(5) linking. These facts are in good agreement with the hypothesis we made concerning the form of structural water (H_2O molecules rather than OH groups).

TABLE IV

INTERATOMIC DISTANCES (Å) IN $WO_3 \cdot \frac{1}{3}H_2O$

W(1) Octahedron	
W(1)–O(1)	1.9
W(1)–O(2)	1.9
W(1)–O(3)	1.9
W(2) Octahedron	
W(2)–O(2)	1.9
W(2)–O(4)	2.1
W(2)–O(5)	1.8

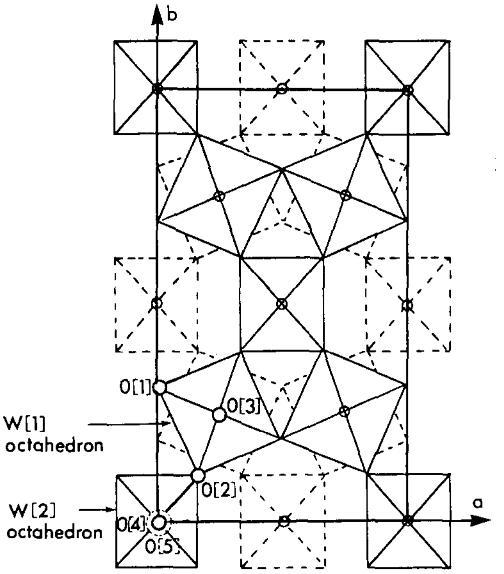

FIG. 7. Schematic projection of the crystal structure of $WO_3 \cdot \frac{1}{3}H_2O$ parallel to [001].

Conclusion

We have obtained a new tungsten trioxide hydrate, $WO_3 \cdot \frac{1}{3}H_2O$. This hydrate cannot be obtained by dehydration in air of the known mono- or dihydrate. It is prepared pure only by hydrothermal treatment at 120°C of an aqueous suspension of either tungstic acid gel or well-crystallized $WO_3 \cdot 2H_2O$.

$WO_3 \cdot \frac{1}{3}H_2O$ was characterized by several methods and its structure determined from X-ray powder diffraction data. There is a structural filiation between the parent phase ($WO_3 \cdot \frac{1}{3}H_2O$) and the product phase of dehydration (WO_3). This explains why dehydration of this hydrate leads to a new anhydrous tungsten trioxide: hexagonal WO_3. In this way $WO_3 \cdot \frac{1}{3}H_2O$ must be regarded as an interesting compound, the chemistry of hexagonal WO_3 appearing full of promise (*13–14*).

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