



A study of the crystal structure of pervanadyl trimethoxide
by Walter A Ryder

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemistry at Montana State College
Montana State University
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Abstract:

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ABSTRACT

Pervanadyl trimethoxide has been prepared. The crystal belongs to the monoclinic system. Tentative unit cell dimensions are: "a"sin β = 15.2 \pm .2 A., "b" = 15.9 \pm .2 A., "c" = 9.9 \pm .4 A. The space group to which the crystal belongs is tentatively identified as either P2₁/m or P2₁.

INTRODUCTION

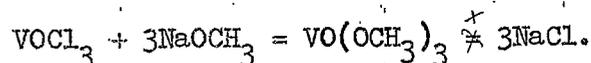
Many of the properties of a crystalline substance are dependent upon its crystal structure. In studying a new or little known compound, therefore, a knowledge of its crystal structure would be of value in predicting and explaining observed properties. Before one can determine the actual positions of the atoms in the crystal by x-ray diffraction, one must have a knowledge of the unit cell dimensions, the space group, and the indices of the reflecting planes. The primary objective of this thesis was to obtain this preliminary information.

There are several different x-ray techniques that are used in crystal structure studies. The equipment available limited the possible techniques to be used in this study to the oscillating and rotating crystal methods. A number of difficulties were encountered along the way which further limited the work to a study of a single rotation pattern.

PREPARATION OF $\text{VO}(\text{OCH}_3)_3$

Several of the esters of orthovanadic acid have been known for a long time and are described in the literature. No successful preparation of the methyl ester is described, however. Hall (5) attempted to prepare it by heating silver orthovanadate and methyl iodide without success. Prandlt and Hess (9) tried refluxing methanol and V_2O_5 , also without success. These are the only references to this ester that were found.

The method used to make the methyl ester is that used by Cartan and Caughlan (4) to make the ethyl ester. The reaction involved is as follows:



Approximately 300 ml of absolute methanol was further dried with magnesium turnings and then distilled. It was placed in a 3-necked, 1000 ml flask equipped with a mercury sealed stirrer, dropping funnel, and a condenser. The flask was cooled in a water bath, and 20 grams of sodium metal cut into small pieces, added. The resulting solution of sodium methoxide was kept in the water bath, and 25 ml of VOCl_3 added drop by drop through the dropping funnel. The reaction was very violent and a yellow gas appeared in the reaction vessel. At the end of the addition the reaction mixture consisted of a yellow solid material and a red liquid. With the addition of heat some of the solid material dissolved. After refluxing for one hour the material was centrifuged and the supernatant liquid poured off and stored in the refrigerator. The crystals of pervanadyl trimethoxide precipitated from this solution on cooling. Additional crops of crystals

were obtained from the residue of the centrifuge process by extracting with methanol. The crystals were purified by repeated recrystallization from methanol until a negative test for chloride ion was obtained. They were stored in the refrigerator covered with methanol.

ANALYSIS

The identification of the crystals is based upon the analysis for their vanadium content. The procedure is that used by Cartan and Caughlan (4).

The alcohol was removed from the crystals by suction filtration, and the crystals immediately placed in a weighing bottle in a vacuum desiccator where they were kept under vacuum until a constant weight was obtained. The samples were then weighed into 250 ml erlenmeyer flasks containing 10 ml of water and 3 ml of concentrated H_2SO_4 . After they were completely dissolved, the volume of the contents was brought to about 75 ml with distilled water and then heated to boiling to remove any alcohol. After cooling, excess Na_2SO_3 was added to each flask which was then allowed to stand for several hours to insure complete reduction. The contents were then boiled for three minutes while a stream of nitrogen was passed through the flask to prevent air oxidation and to sweep out excess SO_2 . The samples were titrated immediately while hot with standardized permanganate solution. The results showed a vanadium content as follows: 31.84%, 32.26%, 32.05% and 32.42%. The theoretical value is 31.83%.

GROWING AND MOUNTING THE CRYSTAL

Pervanadyl trimethoxide crystallizes from methanol in the form of yellow, needle-like crystals, most of which are from 1 to 2 mm long. Under the polarizing microscope it was found that the smaller crystals gave complete extinction indicating that they were single crystals. Most of the larger crystals, however, did not give complete extinction but merely dimmed at certain angles. These were thought to be multiple crystals.

At first, attempts to mount the smaller crystals on the goniometer were made. In an attempt to prevent decomposition, the crystals were coated with stopcock grease and with paraffin. The warm paraffin dissolved the crystals and the stopcock grease did not prevent decomposition. Placing the crystals in sealed, thin-wall, glass capillaries was tried next. Single crystals were selected by observation with the microscope, picked up on the end of a needle, and placed in the capillary which was then sealed in a flame. These crystals always decomposed in a short while, even though the capillaries were dried in an oven and a stream of dry CO_2 from dry ice was directed over the work area during the selection of the crystal. It was finally found that the decomposition could be slowed down considerably by placing a small amount of methanol in the bottom of the capillary, and sticking the crystal to the wall of the tube with a small amount of silicone stopcock grease.

While attempts to mount one of the small crystals were being made, a method of growing crystals with more suitable breadth was considered. Re-

crystallization from different solvents was tried without success. Benzene, heptane, and n-propyl alcohol were used. The crystals obtained were smaller than those from methanol. Small amounts of heptane and benzene were then added to saturated methanol solutions which were then cooled. The resulting crystals were no larger than ordinary. The slow cooling of a saturated solution in a flask was then tried, but the method of controlling the cooling was not satisfactory and no larger crystals were obtained.

Slow evaporation of methanol solutions was also tried. First, a small flask of the solution was placed in an empty desiccator and a stream of N_2 , that had been run through a $CaCl_2$ drying tube and then a $CaSO_4$ drying column, was passed through. This merely deposited a powder-like material on the walls of the flask. Three small flasks of the solution were then connected in series, and a slow stream of dry N_2 run through them. It was hoped that the N_2 would become almost saturated with alcohol vapor from the first two flasks and that the rate of evaporation from the last one would be very slow. Negative results were again obtained.

The only successful method found was that of growing the crystals in capillaries kept in a thermostat. Crystals were dissolved in methyl alcohol by heating the solution drawn into the capillaries which were then sealed at both ends and placed in a test tube in the $25^{\circ}C$ thermostat. In a few of the capillaries single crystals of the desired size grew in clusters at the bottom. These were detached with a fine glass probe drawn from glass rod stock, and then drawn into a smaller capillary. The presence

of other loose crystals made the separation a little more difficult.

Some of the capillaries that did not produce crystals in the 25°C thermostat were placed in a cold water bath. A few of these produced crystals that were about .5 cm long, and very thin, growing in clusters. In one tube there was a cluster of crystals at the top and at the bottom. Joining the two clusters was a thread-like crystal about 2 cm long that gave complete extinction. The center portion of this crystal appeared to be straight although it was bent near the ends. All but a small amount of the alcohol solution was drained off and the tube resealed. It was then mounted on the goniometer so that the x-ray beam passed through the straight portion of the crystal. A four hour rotation picture was taken. The resulting pattern was the only successful single crystal picture that was taken before the x-ray equipment broke down. This is the pattern that has been indexed.

INDEXING

The first attempts at indexing were made on the powder pattern. A crystal had been previously mounted on the goniometer and six reflections noted about 60° apart. This seemed consistent with the faces noted on a large crystal observed under the microscope. For these reasons the crystal symmetry was presumed to be hexagonal and an analytical method for indexing (6) was tried. This left several lines unaccounted for, so the graphical method using Hull-Davey charts (5) was tried. The same results were obtained.

It was then decided to attempt the indexing on the basis of orthorhombic symmetry. There appeared to be a 90° angle between the lateral faces and the terminal faces of the crystal, and the parallel extinction expected for orthorhombic crystals was noted. The analytical method for the orthorhombic system was tried again and possible indices obtained for all the prominent lines. The indexing of the zero level of the rotation pattern was then tried using the graphical method described by Bunn (3). Some of the spots fitted exactly, while others were only close. It was possible to determine the 200 and the 020 spots with certainty, however. From these spots the length of the "a" and the "b" axes can be determined: The interplanar spacing of each spot is calculated from the Bragg equation using the angles measured from the film. Because the intercept of the 200 plane is at the midpoint of the "a" edge of the unit cell, and the 020 intercept is at the midpoint of the "b" edge, the lengths of these two edges are

obtained by multiplying the interplanar spacings of the respective spots by two. The length of the "c" edge is obtained by measuring the height of the layer lines on the rotation pattern from the zero level and using the relationship:
$$c = n \frac{\lambda}{\sin \tan^{-1}(y/r)}$$
, where n is the number of the layer line, r is the effective radius of the camera, and λ is the wave length of the x-radiation used.

Using the unit cell dimensions as calculated by the above methods, the reciprocal lattice was constructed and the indexing of the remaining spots on the rotation pattern attempted. The zero layer was completely indexed, but several prominent spots on the other layers could not be accounted for. Shortly after this some crystals were examined with the polarizing microscope and it was observed that in addition to parallel extinction, it occurred at an angle of about 10° or 12° . This identifies the symmetry of the crystal as being monoclinic.

The indexing of a powder pattern of a monoclinic crystal is not possible unless the unit cell dimensions and the angle β between the "a" and the "c" axes are known. The indexing of the zero layer line of a rotation pattern is possible by the graphical method of Bunn if the crystal has been rotated about the "a" or "c" axis. If the monoclinic crystal has been elongated along its "b" axis, it shows consistent parallel extinction. Because this was not observed for these crystals, it is presumed that the rotation was around the "a" or "c" axis.

Since the data and the graph used for indexing the monoclinic system are the same as those used for the orthorhombic system, the results are the

same. Therefore, the 200 and the 020 spots are the same. The lengths of the "b" and "c" axes are still the same as determined before. The 200 plane, however, determines the length of "a" $\sin \beta$. The values obtained were: "a" $\sin \beta = 15.2 \pm .2A$., "b" = $15.9 \pm .2A$., "c" = $9.9 \pm .4A$.

The indices of the remaining spots on the zero level were obtained by constructing the reciprocal lattice of the zero level. The other levels are offset from the zero level by an amount dependent upon the angle β , the value of which is not known. It appeared from the photograph that the four spots, numbers 37, 44, 120, and 131 in figure 2, should have indices differing only, possibly, in sign. The amount of offset of the second levels containing these spots was adjusted arbitrarily until this index number was found. This led to the amount of offset of the other layers, and thus, possible indices were obtained for the remaining spots in the pattern. These are shown in Table I.

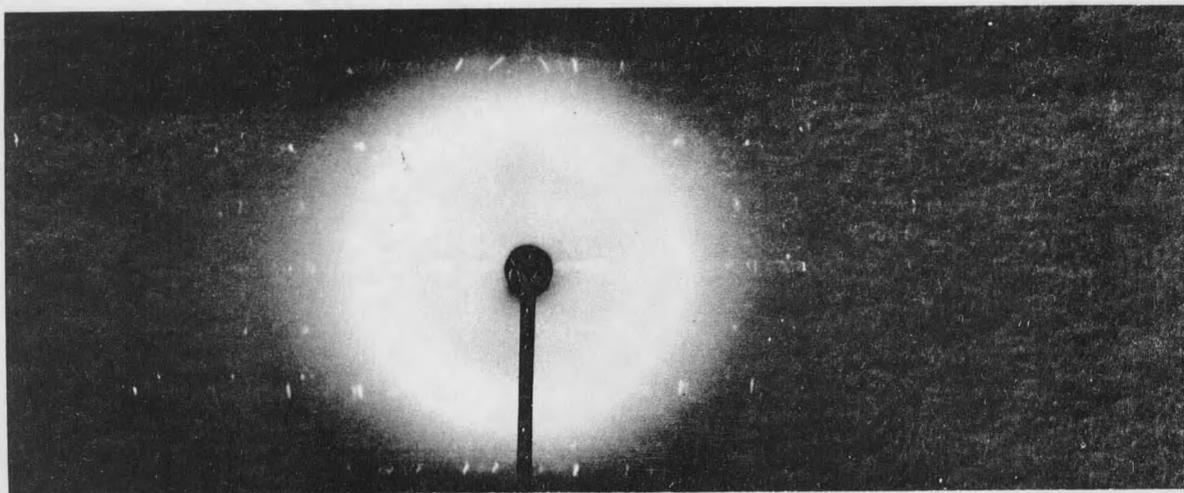


Figure 1. Rotation pattern of Pervanadyl trimethoxide.



Figure 2. Tracing of reflections shown in figure 1. Indices of these reflections are listed in table I.

TABLE 1. Possible Indices of Reflections Shown in Figure L

(Reflection number refers to figure 2.)

Reflection Number	Possible Indices	Reflection Number	Possible Indices
1.	$\bar{2}83, \bar{4}73, 283$ $743, 083$	22.	323
2.	$\bar{3}73, \bar{7}13, \bar{6}43$ 373	23.	$\bar{2}33$
3.	$\bar{3}63, \bar{5}43, 363$	24.	043
4.	$\bar{4}53, \bar{6}13, 363$	25.	143, 413
5.	$\bar{4}33, \bar{3}43$	26.	243
6.	$\bar{2}43$	27.	243
7.	$\bar{3}33, 423$	28.	363
8.	143, 413	29.	373, $\bar{6}43$
9.	043	30.	$\bar{4}122, \bar{6}112,$ $\bar{1}072, \bar{1}212$
10.	$\bar{2}33$	31.	$\bar{9}62, \bar{5}102$
11.	323	32.	$\bar{2}102, 682$
12.	133		
13.	$\bar{2}23$		772
14.	$\bar{2}23$	33.	$\bar{2}82, 742,$ 802
15.	023, 203	34.	742, $\bar{7}32, \bar{5}62$
16.	?	35.	$\bar{2}62$
17.	113	36.	$\bar{1}62$
18.	113	37.	332, 242
19.	?	38.	$\bar{2}42$
20.	203	39.	$\bar{1}22$
21.	033		

40.	012	65.	$\bar{3}01, 131,$ $\bar{1}31$
41.	012	66.	351, 531, 061
42.	242	67.	$\bar{6}41, 721$
43.	332	68.	$\bar{5}71, 651,$ $\bar{7}31$
44.	212, 122	69.	$\underline{1001}, \underline{1011}$
45.	$\bar{1}62$	70.	$\underline{1101}, \underline{1111},$ $\underline{1051}, 881$
46.	042	71.	$\underline{1201}, \underline{1211},$ $\underline{1151}, \underline{1071},$ $6\underline{111}, 4\underline{121}$
47.	1002	72.	$\underline{1141}, \underline{1331},$ $5\underline{131}, 7\underline{121}$
48.	$\bar{4}\underline{111}, \bar{9}71$	73.	$7\underline{141}, \underline{1461}$
49.	681, $2\underline{101}, 941$	74.	$\underline{1120}, \bar{9}70$ $\bar{6}\underline{100}, \bar{4}\underline{110}$
50.	$\bar{9}41, \bar{7}71, \bar{8}61$	75.	$\bar{8}10, \bar{7}40$ $\bar{3}80$
51.	$\bar{4}91, \bar{8}51, 491$	76.	$\bar{4}50, \bar{5}40, \bar{6}20$
52.	471	77.	$\bar{6}10, \bar{4}50, \bar{2}60$
53.	$\bar{6}41, 721$	78.	$\bar{4}40, \bar{3}50$
54.	061, $\bar{3}51, 531$	79.	$\bar{5}20$
55.	$\bar{1}31, \bar{3}01, 131$	80.	$\bar{2}40, \bar{3}30, \bar{4}10$
56.	031	81.	$\bar{1}40, \bar{4}00$
57.	?	82.	$\bar{3}20, \bar{2}30$
58.	$\bar{2}11$		
59.	?		
60.	102		
61.	$\bar{1}11$		
62.	211		
63.	?		
64.	031		

83.	?	108.	$\bar{2}11, 121$
84.	$\bar{2}10$	109.	$21\bar{1}$
85.	$\bar{1}20$	110.	$30\bar{1}, \bar{1}3\bar{1}$
86.	$\bar{2}00$	111.	$35\bar{1}$
87.	020	112.	$72\bar{1}, 37\bar{1}, \bar{6}41$ 641
88.	β	113.	$\bar{1}2\bar{2}\bar{2}$
89.	β	114.	$\bar{1}0\bar{6}\bar{2}, \bar{5}\bar{1}\bar{1}\bar{2}$
90.	β		$\bar{2}\bar{1}\bar{2}\bar{2}$
91.	β	115.	$\bar{1}\bar{1}\bar{2}\bar{2}, \bar{1}\bar{1}\bar{2}\bar{2}$
92.	020		
93.	200	116.	$\bar{2}\bar{1}\bar{0}\bar{2}, \bar{6}\bar{8}\bar{2}, \bar{9}42$
94.	120	117.	$\bar{4}\bar{7}\bar{2}, \bar{2}\bar{8}\bar{3}$
95.	210	118.	$612, \bar{4}52, 262$
96.	140, 400	119.	$\bar{2}\bar{6}\bar{2}$
97.	240, 330, 410	120.	$33\bar{2}$
98.	610, 450, 260	121.	$\bar{2}\bar{4}\bar{3}$
99.	450, 540, 620	122.	$\bar{3}\bar{2}\bar{2}$
100.	370	123.	$\bar{2}\bar{3}\bar{2}$
101.	$\bar{7}\bar{2}\bar{1}, 641$	124.	$12\bar{2}$
102.	$\bar{3}\bar{5}\bar{1}, 441$	125.	$11\bar{1}$
103.	$\bar{3}0\bar{1}, \bar{1}\bar{3}\bar{1}$	126.	?
104.	$03\bar{1}$	127.	111
105.	211	128.	$1\bar{2}\bar{2}$
106.	$\bar{2}\bar{1}\bar{1}, 121$	129.	$3\bar{2}\bar{2}$
107.	?	130.	$2\bar{4}\bar{3}$

131. $3\bar{3}\bar{2}$
132. $2\bar{6}\bar{2}$
133. $6\bar{4}\bar{2}, 7\bar{1}\bar{2}$
134. $4\bar{7}\bar{2}$
135. $2\bar{1}\bar{0}\bar{2}, \bar{6}\bar{8}\bar{2}$
136. $0\bar{1}\bar{1}\bar{2}, \bar{6}\bar{9}\bar{2}, 7\bar{8}\bar{2}$
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137. $\bar{6}\bar{3}\bar{3}, 3\bar{6}\bar{3}, 5\bar{4}\bar{3}, 6\bar{2}\bar{3}$
138. $2\bar{4}\bar{3}$
139. $0\bar{4}\bar{3}, 3\bar{2}\bar{3}, \bar{4}\bar{0}\bar{2}$
140. $2\bar{3}\bar{3}$
141. $0\bar{3}\bar{3}, \bar{3}\bar{0}\bar{3}$
142. $\bar{2}\bar{0}\bar{3}$
143. $1\bar{1}\bar{3}$
144. $\bar{1}\bar{1}\bar{3}$
145. $\bar{1}\bar{1}\bar{3}$
146. $\bar{1}\bar{1}\bar{3}$
147. $\bar{2}\bar{0}\bar{3}$
148. $0\bar{3}\bar{3}, \bar{3}\bar{0}\bar{3}$
149. $2\bar{3}\bar{3}$
150. $\bar{4}\bar{0}\bar{3}, 0\bar{4}\bar{3}, 3\bar{2}\bar{3}$
151. $2\bar{4}\bar{3}$
152. $\bar{6}\bar{3}\bar{3}, 3\bar{6}\bar{3}, 5\bar{4}\bar{3}$
 $6\bar{2}\bar{3}$
153. $7\bar{1}\bar{3}, 6\bar{4}\bar{3}, \bar{3}\bar{7}\bar{3}$

