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The Crystal Structure of $NbOCl_3$*

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$NbOCl_3$ crystallizes in the tetragonal space group, $P4_2/mnm$. There are four formula units in the unit cell with $a_0 = 10{\cdot}87$ and $c_0 = 3{\cdot}96$ Å. This compound forms peculiar polymeric chains of $NbOCl_3$ dimers. The dimer has the same shape as the $NbCl_5$ dimer which has been described as two octahedra sharing an edge. These $NbOCl_3$ dimers form infinite linear chains along the c_0 direction through Nb–O–Nb bonds.

Introduction

The interesting molecular dimerization found in solid $NbCl_5$ (Zalkin & Sands, 1958) has prompted the study of other compounds of niobium and chlorine. $NbOCl_3$ is a co-product in the synthesis of $NbCl_5$ and like $NbCl_5$ is volatile and can be sublimed, but at slightly higher temperatures.

Experimental

Samples of niobium oxychloride were prepared by the reaction of an excess of Nb_2O_5 with CCl_4 (Remy, 1956); $NbCl_5$ and $NbOCl_3$ are both produced in the reaction. $NbCl_5$ is more volatile and was distilled away from the $NbOCl_3$ at 100 °C. in vacuo. At 200 °C., $NbOCl_3$ was distilled from the unreacted oxide. The product is hygroscopic with a fibrous appearance resembling white 'cotton-batting'; this was transferred in an argon-filled dry box to 0·3 mm. quartz capillaries. Crystals suitable for diffraction studies were obtained by heating these capillaries to about 350 °C. and cooling slowly to room temperature. The crystals of $NbOCl_3$ tend to grow into long, slender, colorless needles; twinning could not be avoided.

Oscillation and Weissenberg photographs of a single crystal of $NbOCl_3$ revealed a tetragonal unit cell with:

$$a_0 = 10{\cdot}87 \pm 0{\cdot}01, \quad c_0 = 3{\cdot}96 \pm 0{\cdot}01 \text{ Å}.$$

Four $NbOCl_3$ formula units per unit cell result in a calculated density of 3·04 g.cm.$^{-3}$. The diffraction symmetry and systematic extinctions were characteristic of space groups $P4_2nm$, $P\bar{4}n2$, and $P4_2/mnm$. It was also observed that $hk0$ reflections with $h = 4n$ were weak or missing unless $k = 4n$. Furthermore, the general pattern of the diffraction spots corresponding to the $hk0$ reflections was repeated on all layers with l even, and the pattern of the hkl reflections was repeated on all l odd layers.

The specimen of $NbOCl_3$ on which intensity measurements were made consisted of a bundle of three crystals, each approximately 0·02 mm. in diameter, aligned about a common c_0 axis. A series of rotation pictures were taken with Mo $K\alpha$ radiation, with exposures ranging from one to fifty-four hours. The intensity measurements were made on rotation rather than Weissenberg photographs to avoid the resolution difficulties resulting from the use of a crystal triplet. The intensities were measured by visual comparison with a standard scale, only those reflections being included that could unambiguously be identified on the films. A total of 61 independent intensities were recorded, from the layer lines 0 through 3. To these were added 39 reflections which were too weak to be observed on long-exposure Weissenberg films taken with Cu $K\alpha$ radiation, giving a total of 100 reflections to be included in the least-squares refinements.

The intensities of the $hk0$ reflections from a single crystal 0·05 mm. in diameter, recorded on a Weissenberg film made with Cu $K\alpha$ radiation, were also measured. No absorption corrections were made.

Determination of structure

The very weak intensities recorded for $hk0$ reflections with $h = 4n$, $k \neq 4n$ suggested a niobium atom position of $\frac{1}{8}, \frac{1}{8}, z$. The similarity of the diffraction patterns of all layers with $l = 2n$, and also of all layers with $l = 2n+1$, further suggested that z should be 0 or $\frac{1}{2}$. In terms of space group $P4_2/mnm$, this corresponds to the niobiums occupying positions $4f$: $\pm(x, x, 0; \frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2})$ (*International Tables for X-ray Crystallography*, 1952).

The Fourier projection $\varrho(x, y)$ was computed using the signs of the structure factors computed from these niobium positions and the $hk0$ data obtained from the Weissenberg film made with Cu $K\alpha$ radiation. The chlorine atoms were revealed by this projection to be occupying the $P4_2/mnm$ positions $8i$: $\pm(x, y, 0; y, x, 0; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}; \frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2})$ with $x = 0{\cdot}34$, $y = 0{\cdot}18$, and $4g$: with $x = 0{\cdot}10$. The structure at this stage thus consisted of planar Nb_2Cl_6 groups with two of the chlorine atoms involved in bridge bonds.

The positions of the oxygen atoms were not indicated by the $\varrho(x, y)$ projection, except possibly as an explanation for the relatively high electron density

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Table 1. *Observed and calculated structure factors for* $NbOCl_3$

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
200	<17	< 1	640	< 7	< 1	10,2,1	82	−83	622	<39	16
400	462	−462	740	<43	− 2	531	105	110	722	63	−15
600	<36	−21	840	136	−127	631	54	−51	822	<45	−10
800	163	163	940	<49	8	731	41	−33	922	88	−78
210	203	−212	10,4,0	<52	−21	441	<35	−34	432	<34	−15
310	70	−88	650	132	−130	541	176	174	532	49	55
510	181	−169	750	45	−40	641	<40	4	632	63	65
610	150	156	850	<47	−20	651	<42	− 7	732	61	−55
810	<43	27	950	118	−114	761	<46	16	832	<46	− 4
910	101	95	860	<49	20	861	<49	12	442	204	216
10,1,0	99	−89	960	73	66				542	<39	16
220	<24	−19				202	<21	< 1	642	<21	< 1
420	<31	9	101	272	260	402	290	−296	742	<45	− 2
520	200	196	301	106	−129	602	<38	−14	842	92	−96
720	<40	−17	111	173	−180	802	122	120	552	140	135
820	<44	−13	211	34	−38	112	120	99	652	90	−95
920	115	−103	311	92	−107	212	141	−130	852	<49	−14
10,2,0	<50	− 9	411	161	−164	312	60	−59			
430	<33	−25	511	116	124	512	105	−114	303	77	−66
530	80	79	611	48	45	612	97	108	313	62	−54
630	89	94	10,1,1	<49	−11	812	<45	19	413	76	−85
730	72	−75	221	87	26	912	68	72	513	51	66
830	<44	− 5	421	<31	20	222	<25	−11	333	49	− 7
930	63	−47	521	<34	13	322	69	−38	533	52	60
10,3,0	76	−79	721	<40	− 7	422	<32	6	543	82	97
440	309	314	921	<46	− 3	522	124	135			

found at the sites of the niobium atoms. However, the tendency of the $NbOCl_3$ crystals to grow as fibers along c_0 supported the conclusion that the planar Nb_2Cl_6 groups are joined by Nb–O–Nb bonds parallel to c_0. In terms of space group $P4_2/mnm$, this corresponds to oxygen positions $4g$: $\pm(x,\bar{x},0;\ \frac{1}{2}+x,\frac{1}{2}+x,\frac{1}{2})$, with $x = \frac{3}{8}$.

These atomic positions were refined by successive applications of the least-squares method. Individual isotropic temperature factors were assigned to each atom and were included in the refinements. Separate scale factors for each layer were also included. The value of the reliability coefficient, $R=\Sigma|F_o-F_c|/\Sigma|F_o|$, was 0·071 at the end of the refinements. When the oxygen atoms were omitted, the structure could be refined to an R of 0·080.

The observed and calculated values of the structure factors included in the calculations are listed in Table 1. In Table 2 are the final values of the atomic parameters, including the temperature factors resulting from the least-squares refinements. The standard deviations of the parameters were evaluated by the method of Cruickshank (1949).

Table 2. *Atomic parameters in* $NbOCl_3$

Positions	Atom	x	y	z	B (Å²)
$4f$	Nb	0·127±0·001	0·127±0·001	0	3·0
$4g$	Cl_A	0·104±0·003	0·896±0·003	0	3·2
$8i$	Cl_C	0·331±0·002	0·105±0·002	0	3·3
$4g$	O	0·385±0·007	0·615±0·007	0	3·0

Discussion of structure

The molecular structure of $NbOCl_3$ consists of planar Nb_2Cl_6 groups joined by Nb–O–Nb bonds into infinite chains parallel to c_0. This structure, in which the niobium atoms are connected by chlorine bridge bonds, is shown in Fig. 1. The packing arrangement of the chains is shown in Fig. 2. Table 3 lists the interatomic distances in $NbOCl_3$. The standard deviations of these

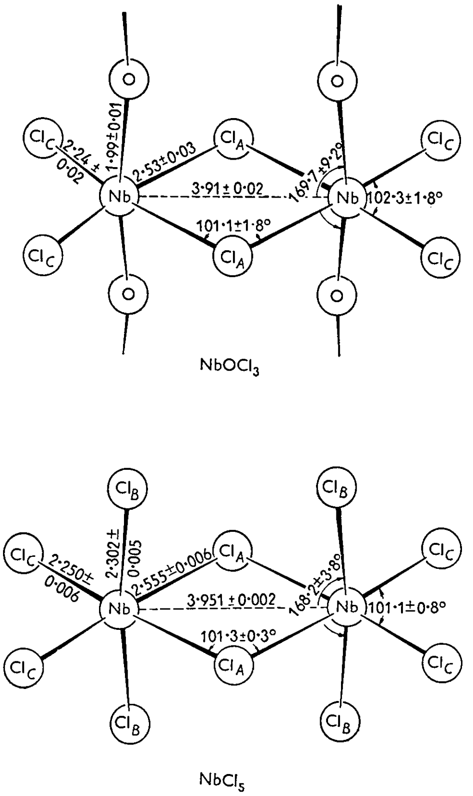

Fig. 1. The molecular configuration of $NbOCl_3$ and $NbCl_5$.

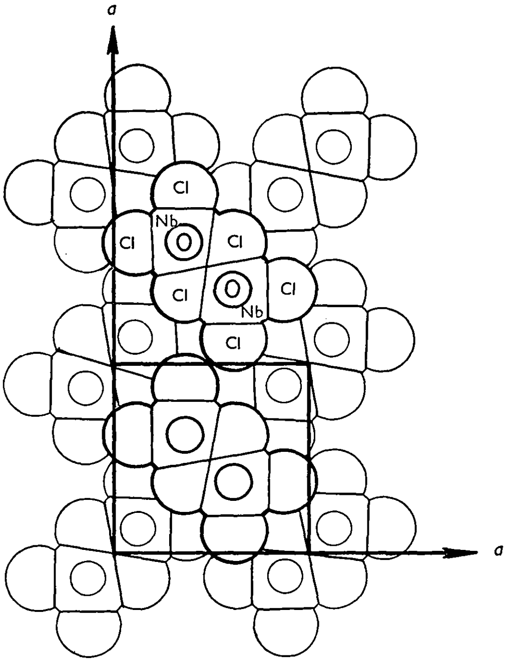

Fig. 2. Packing arrangement in $NbOCl_3$.

distances were computed from the standard deviations of the atomic parameters by the method of Cruickshank & Robertson (1953).

The planar Nb_2Cl_6 groups are also present in crystalline niobium pentachloride (Zalkin & Sands, 1958). The molecular structure of this compound is shown in Fig. 1. In the case of niobium pentachloride, in which the molecular unit is Nb_2Cl_{10}, the planarity of the Nb_2Cl_6 group is not required by the space group, but it is planar to within the precision of the parameters. The molecular symmetry of both Nb_2Cl_{10} and $NbOCl_3$ is D_{2h}–*mmm*.

The four Nb–Cl_B bonds of niobium pentachloride are not perpendicular to the plane of the Nb_2Cl_6, but are bent toward each other to form an angle of about 84° with a line drawn through the two niobium atoms. The parameters produced by the least-squares refinements of the $NbOCl_3$ data suggest a corresponding lack of linearity of the Nb–O–Nb bond. The bending of these bonds may be attributed to the steric effect of the chlorines in the planar Nb_2Cl_6 group, the final position of Cl_B in $NbCl_5$ and of O in $NbOCl_3$ being nearly equidistant from atoms Cl_A and Cl_C; these distances (3·3 and 3·1 Å) are less than the normal van der Waals distances (3·6 and 3·2 Å).

Table 3. *Interatomic distances in* $NbOCl_3$

Nb–2 Cl_A	2·53 ± 0·03 Å	Bridge bond
–2 Cl_C	2·24 ± 0·02	
–2 O	1·99 ± 0·01	
–Nb	3·91 ± 0·02	
Cl_A–2 Nb	2·53 ± 0·03 Å	Bridge bond
– Cl_A	3·22 ± 0·05	
–2 O	3·11 ± 0·06	
–2 Cl_C	3·36 ± 0·04	
–4 Cl_C	3·80 ± 0·03	Intermolecular
Cl_C– Nb	2·24 ± 0·02 Å	
–2 O	3·08 ± 0·06	
– Cl_A	3·36 ± 0·04	
– Cl_C	3·49 ± 0·03	
–2 Cl_A	3·80 ± 0·03	Intermolecular
–4 Cl_C	3·64 ± 0·03	Intermolecular
O–2 Nb	1·99 ± 0·01 Å	
–2 Cl_A	3·11 ± 0·06	
–4 Cl_C	3·08 ± 0·06	
– O	3·55 ± 0·11	

The structure of gaseous $NbOCl_3$ is not known. However, vapor density measurements indicate that the formula of the gaseous molecules is $NbOCl_3$ (Remy, 1956).

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