The Crystal Structure of NbCl₅*

By Allan Zalkin and Donald E. Sands

University of California Radiation Laboratory, Livermore, California

NbCl₅ crystallizes in the monoclinic system with $a = 18\cdot30$, $b = 17\cdot96$, $c = 5\cdot888$ Å, $\beta = 90\cdot6°$. The space group is $C2/m$, and there are 12 NbCl₅ units in the unit cell. The structure consists of dimers (Nb₂Cl₁₀) with the chlorine atoms forming two octahedra which share a common edge. The niobium atoms occupy the centers of the octahedra and are joined by two chlorine bridge bonds. The Nb–Cl bridge bond length is 2·56 Å; the Nb–Cl non-bridge bond lengths are 2·25 and 2·30 Å. NbBr₅ and TaCl₅ appear to be isomorphous with the above structure.

Introduction

Skinner & Sutton (1940) found by means of electron diffraction, trigonal bipyramid units of NbCl₅ and NbBr₅ in the vapor phase. The present investigation was undertaken to study the structure in the crystalline state and to compare it with that reported in the gaseous state.

Experimental

The niobium pentachloride samples were prepared in this laboratory. Nb₂O₅ was reacted with CCl₄ (Remy, 1956); the resulting yellow NbCl₅ was sublimed out from the reaction mixture at a temperature near its melting point (220 °C.). Since the material is extremely hygroscopic, samples of the yellow powder were transferred in an argon-filled dry box to 0·3 mm. quartz capillaries. The sealed capillaries containing the samples were heated to about 230 °C. and cooled over a period of several hours to room temperature; crystals suitable for diffraction studies were thus obtained.

Oscillation, Weissenberg, and precession photographs, using Cu $K\alpha$ radiation ($\lambda = 1\cdot5418$ Å) show a monoclinic unit cell with:

$$a = 18\cdot30\pm0\cdot01, \quad b = 17\cdot96\pm0\cdot02, \quad c = 5\cdot888\pm0\cdot004 \text{ Å},$$
$$\beta = 90\cdot6°\pm0\cdot01°\ .$$

These values agree well with those obtained by Douglass & Staritzky (1957).

The measured density is 2·75 g.cm⁻³ (*Lange's Handbook of Chemistry*, 1949); the density calculated from the above data is 2·78 g.cm.⁻³; there are 12 NbCl₅ formula units per unit cell. The diffraction symmetry and extinction conditions were characteristic of space groups $C2$, Cm, and $C2/m$. Both our crystals and those studied by Douglass & Staritzky (1957) were yellow plates flattened on (010) and elongated in the direction of c_0. The crystals were invariably twinned on (100), sharing a common c_0-axis, and this twinning plus the

proximity of β to 90° frequently made it difficult or impossible to observe the separation of the hkl reflection of one twin from the $\bar{h}kl$ reflection of the other twin. In addition to the hkl, $h+k = 2n$, extinctions required by the space group, it was found that $hk0$ reflections were present only for $h = 3n$. Furthermore, hkl reflections with $l = 2n$ were apt to be weak or missing unless $h = 3n$. Some crystals contained a large amount of disorder in the stacking of planes perpendicular to b_0, manifested as diffuseness and streaking in the direction of b^* of those reflections with $h \neq 3n$.

The specimen selected for the structural investigation was free of stacking disorder. It was a flat plate of approximate dimensions 0·40×0·21×0·09 mm., the unique axis being perpendicular to the plate and c_0 parallel to the long edge. The crystal was oriented about c_0.

The relative intensities of the reflections on the $l = 0, 1, 2$, and 3 equi-inclination Weissenberg layers, made with Cu $K\alpha$ radiation and the usual multiple-film technique, were estimated by visual comparison with a standard scale. Values of $|F|^2$ were obtained by application of the Lorentz, polarization, and velocity factors.

The $hk0$ data were corrected for absorption by the method described by Busing & Levy (1957). The IBM 650 was programmed to compute the absorption as a function of φ and θ which could then be plotted as a template to fit over a Weissenberg film, where φ is the rotation coordinate of the crystal and θ is the Bragg angle.

The intensities of the $h0l$ reflections were visually estimated from precession photographs made with Mo $K\alpha$ radiation. Correction for Lorentz and polarization factors was accomplished with the aid of the chart computed by Waser (1951). No absorption corrections were made in this case.

Determination of the structure

Since it was generally very difficult to resolve an hkl reflection on the Weissenberg films from the $\bar{h}kl$

reflection of its twin, the intensities of these reflections were treated together in the preliminary stages of the investigation. Our measured intensities were therefore proportional to $|F(hkl)|^2 + r|F(\bar{h}kl)|^2$, where r is the ratio of the volumes of the two twins; it was found that r was about 3 in the crystal being studied.

A total of 518 independent combined reflections were observable on the Weissenberg films, and these intensities were used in the computation of the Patterson projection $P(u, v)$ and the Patterson sections $P(u, v, 0)$, $P(u, v, \frac{1}{4})$, and $P(u, v, \frac{1}{2})$. These vector maps indicated that, as a first approximation, the chlorine atoms lie in hexagonal close-packed layers at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, the nearest neighbor distance in the layers being of the order of 3·6 Å, the van der Waal diameter of chlorine. The niobium atoms occur in pairs parallel to the monoclinic axis. The molecular structure based on these considerations consists of ten chlorine atoms arranged at the vertices of two octahedra sharing an edge, with the two niobium atoms at the centers of the octahedra. There are six such Nb₂Cl₁₀ groups within the unit cell. This proposed structure fits the requirements of space group $C2/m$, with the molecules occupying the positions $2a$ and $4i$ (with $x = \frac{1}{8}$, $z = 0.525$).

The parameters obtained from the various Patterson maps were used as the starting point in least-squares refinement of the data. Individual isotropic temperature factors were assigned to each atom and were included in the refinements.

The first set of data to be given the least-squares treatment was the $hk0$ projection. A total of 77 independent reflections, of which 10 were too weak to

be observed, were included in the computation. ($hk0$ reflections with $h \neq 3n$ were considered to be systematically missing and were not included in these refinements.) Before absorption corrections were applied a reliability factor of 18·5% was attained. The absorption corrections resulted in a reduction of the reliability factor to 14·3%, but only slight parameter shifts occurred. The observed $hk0$ structure factors, corrected for absorption, are listed with the calculated values in Table 1. Fig. 1 shows the $\varrho(x, y)$ Fourier projection calculated from these data.
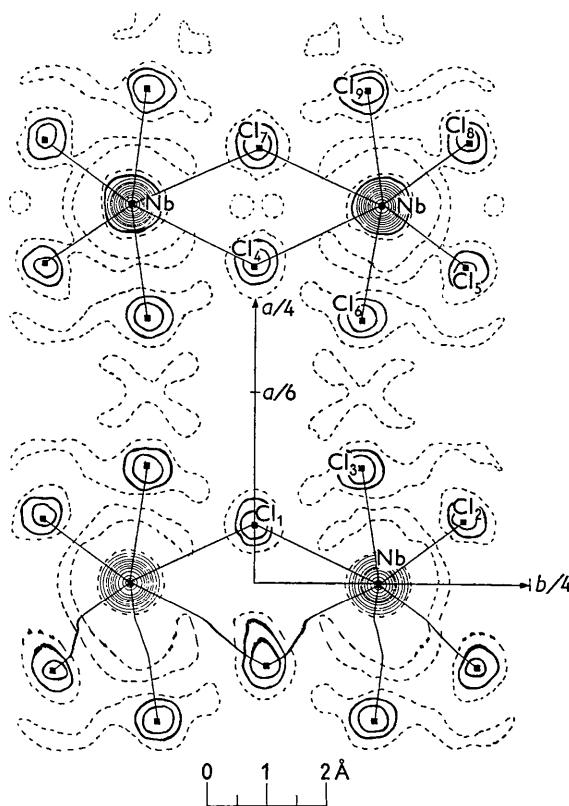

Fig. 1. Electron density projected on (001). The contours are at equal arbitrary intervals; the zero contour is broken; $F(000)$ has not been included.

Table 2 lists the 74 (of which 21 were unobserved) $h0l$ structure factors obtained from a precession photograph. A reliability factor of 14·2% was obtained for this projection. Lack of resolution of the chlorine atoms limited the usefulness of these data to the determination of the parameters of Nb₂. The $\varrho(x, z)$ Fourier projection is shown in Fig. 2.

The z parameters of the Cl atoms were obtained by least-squares refinement of those $hk3$ data for which hkl and $\bar{h}kl$ reflections of the twins were sufficiently separated on the Weissenberg films. The structure factors of 212 independent reflections (of which 62 were unobserved) were included in this refinement, and a reliability factor of 20·6% was obtained. The observed and calculated structure factors are listed in Table 3.

Table 1. *Observed and calculated structure factors for the $hk0$ reflections of* NbCl₅

	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c
	$h = 0$		$h = 6$		$h = 12$		$h = 18$	
$k = 0$			8	$-<1$	19	16	33	36
2	17	13	5	4	6	5	< 3	3
4	46	-46	21	-26	31	-33	12	-15
6	17	-13	17	-14	27	-25	< 3	-3
8	23	18	28	26	23	18	11	10
10	50	62	< 1	< 1	13	9	28	24
12	2	2	22	-18	13	-12	< 2	-3
14	25	-28	15	-15	24	-20	10	-11
16	12	9	< 3	2	5	6		
18	17	16	21	19	16	13		
20	18	17	4	-3				
22	3	-2	14	-16				
	$h = 3$		$h = 9$		$h = 15$		$h = 21$	
$k = 1$	29	42	20	21	11	10	21	20
3	21	-24	16	-12	12	-12	4	-7
5	4	-6	49	-66	< 3	-4	14	-11
7	15	10	< 2	-3	7	6	< 2	3
9	31	31	32	29	11	13	18	18
11	14	13	3	-3	< 1	< 1		
13	24	-24	17	-16	21	-18		
15	2	$-<1$	27	-29	< 2	$-<1$		
17	20	20	2	2	13	13		
19	13	13	16	14				
21	2	-3	9	10				

Table 2. *Observed and calculated structure factors for the h0l reflections of* $NbCl_5$

	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c
	$h = 0$		$h = 2$		$h = 4$		$h = 6$		$h = 8$	
$l = -5$			35	30	8	6	23	17	16	12
-4			18	-15	< 6	1	< 6	4	10	$- 9$
-3			21	20	10	7	40	-39	31	30
-2			< 1	$-< 1$	13	16	56	41	< 6	
-1			28	38	20	25	34	36	18	21
0			< 3	$- 1$	< 2	< 1	8	3	< 6	$-< 1$
1	19	-19	22	29	28	31	60	-60	12	16
2	37	-30	< 1	1	14	-15	61	64	< 6	6
3	< 6	$- 3$	6	4	28	27	23	24	19	17
4	58	60	23	22	< 6	5	< 6	$- 2$	< 6	9
5			< 6	9	26	20	25	-20	< 6	$- 9$

	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c
	$h = 10$		$h = 12$		$h = 14$		$h = 16$		$h = 18$	
$l = -4$			16	14						
-3	12	12	20	14	19	18				
-2	< 6	3	28	28	< 6	$- 6$				
-1	12	16	33	-34	19	16	16	13		
0	< 3	$-< 1$	17	21	< 6	< 1	< 6	$- 2$	17	25
1	19	19	28	18	14	15	23	17		
2	< 6	$-< 1$	25	27	< 6	6				
3	28	28	32	-28						
4	14	-12	20	30						
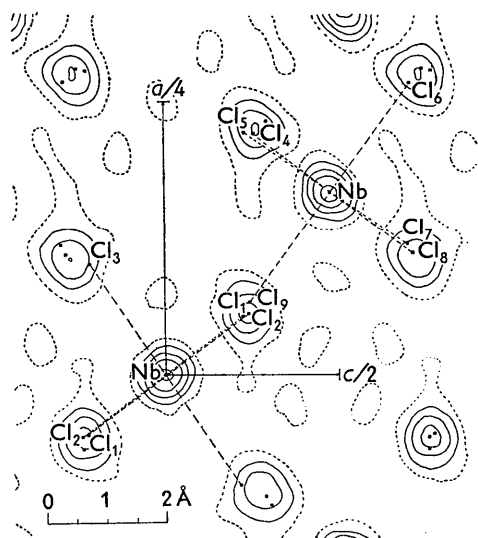
Fig. 2. Electron density projected on (010). The contours are at equal arbitrary units; the zero contour is broken; $F(000)$ has not been included.

The atomic parameters, obtained from the three sets of data, were weighted by the inverse squares of their standard deviations (computed by the method of Cruickshank, 1949) and averaged. The niobium atoms occupy positions $4(g)$ and $8(j)$ of space group $C2/m$ (*International Tables for X-ray Crystallography*, 1952); the chlorine atoms occupy three sets of $4(i)$ and six sets of $8(j)$ positions. These positions are as follows:

$4(g)$ $0, y, 0$; $0, \bar{y}, 0 + C$ centering.

$4(i)$ $x, 0, z$; $\bar{x}, 0, \bar{z} + C$ centering.

$8(j)$ x, y, z; $x, \bar{y}, z$; $\bar{x}, y, \bar{z}$; $\bar{x}, \bar{y}, \bar{z} + C$ centering.

These parameters are listed in Table 4. The isotropic temperature factors given are the unweighted averages of the results of the three least-squares refinements.

Discussion

Two independent configurations of the Nb_2Cl_{10} group are given by the structure, one of which is constrained to $2/m$ symmetry while the other is required to possess only a mirror plane. The Nb–Nb distances of the two molecules agree to within 0.2% and the Nb–Cl distances agree to about 0.5%. Fig. 3 shows this average molecule, and Table 5 lists the distances between nearest neighbors, calculated on the assumption that all Nb_2Cl_{10} molecules are identical and have $2/m$ symmetry. The probable errors in these distances were calculated from the standard deviations in the atomic parameters (Cruickshank & Robertson, 1953). Table 5 also shows the number and type of nearest neighbors for each of the four types of atoms, Nb,
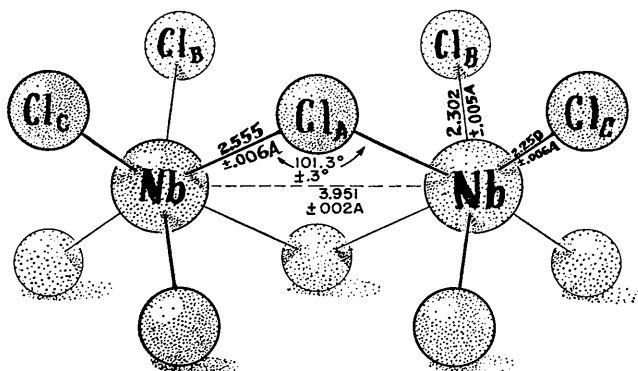

Fig. 3. Configuration of the Nb_2Cl_{10} dimeric molecule in the crystalline state.

Table 3. *Observed and calculated structure factors for the hk3 reflections of NbCl₅*

Table 4. *Atomic parameters in* $NbCl_5$

Position	Atom	x	y	z	B ($Å^2$)
$4(g)$	Nb_1	0.0000	0.1106 ± 0.0006	0.0000	1.0
$8(j)$	Nb_2	0.3333 ± 0.0004	0.1108 ± 0.0004	0.525 ± 0.001	1.4
$4(i)$	Cl_1	0.053 ± 0.002	0.0000	0.225 ± 0.007	1.8
$8(j)$	Cl_2	0.056 ± 0.002	0.191 ± 0.002	0.240 ± 0.006	3.2
$8(j)$	Cl_3	0.103 ± 0.002	0.097 ± 0.002	0.782 ± 0.005	3.0
$4(i)$	Cl_4	0.280 ± 0.002	0.0000	0.744 ± 0.007	2.2
$8(j)$	Cl_5	0.279 ± 0.002	0.189 ± 0.002	0.770 ± 0.006	3.1
$8(j)$	Cl_6	0.232 ± 0.002	0.098 ± 0.002	0.293 ± 0.006	3.2
$4(i)$	Cl_7	0.381 ± 0.002	0.0000	0.298 ± 0.006	1.1
$8(j)$	Cl_8	0.389 ± 0.002	0.190 ± 0.002	0.285 ± 0.006	3.4
$8(j)$	Cl_9	0.434 ± 0.002	0.098 ± 0.002	0.760 ± 0.006	3.3

Table 5. *Nearest neighbor distances in* $NbCl_5$

Nb–1 Nb	3.951 ± 0.002 Å	Intramolecular
–2 Cl_A	2.555 ± 0.006	
–2 Cl_B	2.302 ± 0.005	
–2 Cl_C	2.250 ± 0.006	

Cl_A–2 Nb	2.555 ± 0.006 Å	Intramolecular
–1 Cl_A	3.25 ± 0.02	
–4 Cl_B	$3.30, 3.31 \pm 0.03$	
–2 Cl_C	3.40 ± 0.03	
–5 Cl	$3.68 - 3.83$	Intermolecular (average = 3.76)

Cl_B–1 Nb	2.302 ± 0.005 Å	Intramolecular
–2 Cl_A	$3.30, 3.31 \pm 0.03$	
–1 Cl_B	3.48 ± 0.03	
–2 Cl_C	$3.33, 3.31 \pm 0.03$	
–7 Cl	$3.60 - 3.92$	Intermolecular (average = 3.74)

Cl_C–1 Nb	2.250 ± 0.006 Å	Intramolecular
–1 Cl_A	3.40 ± 0.03	
–2 Cl_B	$3.33, 3.31 \pm 0.03$	
–1 Cl_C	3.49 ± 0.03	
–8 Cl	$3.62 - 3.98$	Intermolecular (average = 3.74)

Cl_A, Cl_B, and Cl_C (see Fig. 3). The packing of these dimers is shown in Fig. 4.
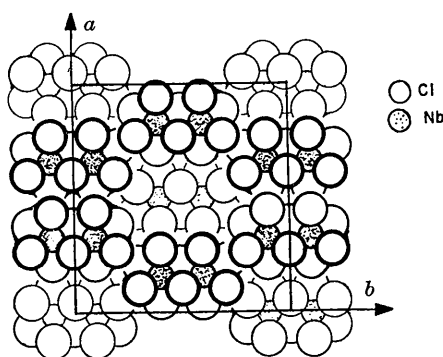

Fig. 4. Packing arrangement of the Nb_2Cl_{10} groups in the crystal of niobium pentachloride.

A comparison of the configuration and size of the molecule in the gaseous and solid state is shown in Table 6.

The distances in the two structures are reasonably equivalent. The molecular formula $NbCl_5$ in the vapor

Table 6. *Comparison of the molecular structure of* $NbCl_5$ *in the gas and solid phases*

	Gas*	Solid
Molecular formula	$NbCl_5$	Nb_2Cl_{10}
Molecular configuration	Trigonal bipyramid	Two octahedra sharing an edge 2.25 ± 0.01 Å
Nb–Cl distances	2.29 ± 0.03 Å	2.30 ± 0.01 2.56 ± 0.01 (bridge bond)
Cl–Cl distances (intramolecular)	3.23 Å	3.25 to 3.48 Å

* Skinner & Sutton (1940) data.

phase is supported by vapor density measurements at 360 °C. (Remy, 1956).

$NbBr_5$ and $TaCl_5$ appear to be isomorphous with $NbCl_5$. Powder patterns of $NbBr_5$ indicate a unit cell of $a = 19.2$, $b = 18.6$, $c = 6.0$ Å, $\beta \approx 90°$. Single-crystal photographs of $TaCl_5$ show a cell which is indistinguishable in size from $NbCl_5$, but with variations in intensities of the reflections.

References

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* 10, 180.
Cruickshank, D. W. J. (1949). *Acta Cryst.* 2, 154.
Cruickshank, D. W. J. & Robertson, A. P. (1953). *Acta Cryst.* 6, 698.
Douglass, R. M. & Staritzky, E. (1957). *Anal. Chem.* 29, 315.
International Tables for X-ray Crystallography (1952), vol. 1. Birmingham: Kynoch Press.
Lange's Handbook of Chemistry (1949). 7th Ed. p. 208. Sandusky, Ohio: Handbook Publishers, Inc.
Remy, H. (1956). *Treatise on Inorganic Chemistry*, vol. 2, p. 109. Amsterdam: Elsevier Publishing Company.
Skinner, H. A. & Sutton, L. E. (1940). *Trans. Faraday Soc.* 36, 668.
Waser, J. (1951). *Rev. Sci. Instrum.* 22, 567.