

717. *The Structures of Niobium and Tantalum Pentafluorides.*

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The pentafluorides of niobium and tantalum have been shown, by *X*-ray single-crystal techniques, to have a tetrameric structural unit in the solid. The metal atoms are at the corners of a square, linked by linear bridging fluorine atoms. The two compounds are isostructural with molybdenum pentafluoride. In each, the metal-fluorine bridging bond length is 2.06 Å and the metal-fluorine non-bridging bond length 1.77 Å.

NIObIUM and tantalum pentafluorides have been known for many years, they were prepared and fully characterised by Ruff and Schiller¹ in 1911. These workers also measured the vapour pressures and densities of the two compounds, as well as investigating many of their chemical reactions. More recently, Fairbrother and his co-workers² have accurately established the melting and boiling points of the pentafluorides, from vapour-pressure measurements, and have also studied the electrical conductivities of the molten compounds.

The properties of the two pentafluorides are very similar. Both are white crystalline solids, m. p. 80°, b. p. 235°, for niobium pentafluoride, and m. p. 95°, b. p. 229° for tantalum pentafluoride; these values are near those of other transition-metal pentafluorides.³ The compounds can be handled and stored in Pyrex glass under rigorously dry conditions.

Crystals were set up in Pyrex glass capillaries for the structure determination, as described below.

EXPERIMENTAL

The two pentafluorides were prepared by direct fluorination of the powdered metals. Purification was achieved by slow sublimation under high vacuum; this treatment removed any traces of hydrogen fluoride, and the purified samples did not attack glass, even after several months at room temperature.

Preparation of Single Crystals.—Both compounds are immediately hydrolysed by moist air and it was necessary to seal the crystals in Pyrex capillaries under vacuum. Samples were sublimed and powdered with nickel balls under high vacuum. Small amounts of the powder were shaken into long capillaries, and these were then sealed from the rest of the apparatus. The capillaries were kept at 60–70° for several days, and well-formed crystals grew on the tube walls. Single crystals were sealed in small sections of capillary by means of a micro flame. This technique was superior to the methods used for molybdenum⁴ and ruthenium⁵ pentafluorides, as the crystals adhered firmly to the glass. Crystals were set about crystallographic axes by the usual methods. Preliminary powder photographs had established that the unit cells of the two compounds were similar to that of molybdenum pentafluoride, and the correct axes were easily identified.

Crystal Values.—NbF₅, $M = 187.9$, monoclinic, $a = 9.62 \pm 0.01$, $b = 14.43 \pm 0.02$, $c = 5.12 \pm 0.01$ Å, $\beta = 96.1 \pm 0.3^\circ$, $V = 706$ Å³, $D_m = 3.29$,¹ $Z = 8$, $D_c = 3.54$, $F(000) = 688$. Space group $C2/m$ (C^{3h}_2 , No. 12). Cu- K_α radiation, single crystal oscillation and Weissenberg photographs.

TaF₅, $M = 275.9$, monoclinic, $a = 9.64 \pm 0.01$, $b = 14.45 \pm 0.02$, $c = 5.12 \pm 0.01$ Å, $\beta = 96.3 \pm 0.3^\circ$, $V = 706$ Å³, $D_m = 4.98$,¹ $Z = 8$, $D_c = 5.19$, $F(000) = 944$. Space group $C2/m$ (C^{3h}_2 , No. 12). Cu- K_α radiation, single-crystal oscillation and Weissenberg photographs.

For both compounds reflections with $h + k \neq 2n$ were systematically absent, characteristic of space groups $C2$, Cm , and $C2/m$. The space group $C2/m$ was confirmed by the success of the analysis. The linear absorption coefficients with Cu- K_α radiation are 299 cm.⁻¹ for niobium pentafluoride and 590 cm.⁻¹ for tantalum pentafluoride.

¹ Ruff and Schiller, *Z. anorg. Chem.*, 1911, **72**, 329.

² Fairbrother and Frith, *J.*, 1951, 3051; Fairbrother, Frith, and Woolf, *J.* 1954, 1031.

³ Cady and Hargreaves, *J.*, 1961, 1568.

⁴ Edwards, Peacock, and Small, *J.*, 1962, 4486.

⁵ Holloway, Peacock, and Small, *J.*, 1964, 644.

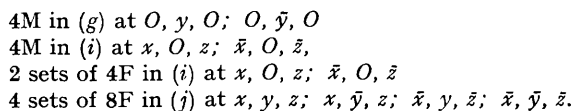
Structure Determination.—Intensity values were collected for the three principal zones for niobium pentafluoride, and for the $hk0$ and $h0l$ zones for tantalum pentafluoride. The usual multiple-film technique was applied, and relative intensities estimated by visual comparison with a standard scale. Values of F^2 were obtained by correction for Lorentz and polarization factors. The spots were small, but not as difficult to estimate as those obtained from molybdenum pentafluoride,⁴ since the background intensity was much lower. This also allowed more spots of lower intensity to be observed. 153 of a possible 196 reflections were observed for niobium pentafluoride and 125 of a possible 155 for tantalum pentafluoride.

Inspection of the intensities showed that the structures of the two compounds were very similar to that of molybdenum pentafluoride. Structure factors were calculated for niobium pentafluoride by using the co-ordinates found for molybdenum pentafluoride. The scattering factors of Thomas and Umeda⁶ were used for niobium, and those of Berghuis *et al.*⁷ for fluorine; values were taken for the un-ionized atoms.⁸

The atomic co-ordinates and temperature factors were refined by the least-squares procedure. The final R values for the zones were: $hk0$, 9.2; $h0l$, 11.9; $0kl$, 9.8% (for observed reflections only). The isotropic temperature factors were $B_{\text{Nb}} = 1.8 \text{ \AA}^2$ and $B_{\text{F}} = 3.8 \text{ \AA}^2$.

Structure factors were calculated for tantalum pentafluoride by using the parameters found for the niobium compound. Thomas and Umeda's⁶ scattering factors were used for tantalum, and a correction was made for dispersion.⁹ Application of an absorption correction, for a cylindrical specimen with $\mu_r = 3.5$,¹⁰ to the observed intensities gave R values: $hk0$, 11.4; $h0l$, 11.8% (for observed reflections only). Since the crystals used were of irregular shape, this agreement was considered satisfactory for the absorption errors involved. The interatomic distances were taken to be the same as in niobium pentafluoride, for the cell dimensions are the same within experimental error.

Results.—In niobium and tantalum pentafluorides the atoms occupy the following positions of space group $C2/m$ ¹¹ (all with C face-centring).



The estimated standard deviations were calculated by Cruikshank's method¹² for niobium pentafluoride. Final atomic parameters with their estimated standard deviation (σ) are given

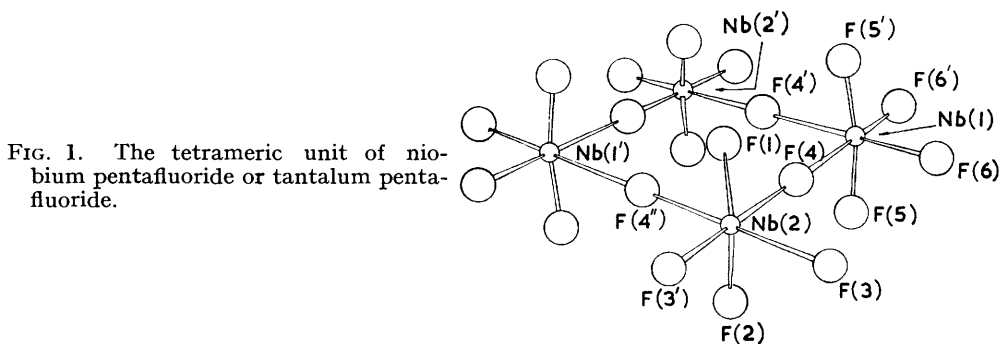


FIG. 1. The tetrameric unit of niobium pentafluoride or tantalum pentafluoride.

in Table 1. Interatomic distances are given in Table 2 for niobium pentafluoride and are the same for tantalum pentafluoride (for which no errors were calculated). Table 3 shows observed and calculated structure factors, and the tetrameric arrangement is illustrated in Fig. 1.

⁶ Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

⁷ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

⁸ Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 244.

⁹ "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, Vol. III, p. 213.

¹⁰ Ref. 9, Vol. II, p. 295.

¹¹ Ref. 9, Vol. I, p. 99.

¹² Cruikshank, *Acta Cryst.*, 1949, **2**, 65.

TABLE 1.
Atomic parameters.

Atom	x/a	y/b	z/c	σ (Å)	Atom	x/a	y/b	z/c	σ (Å)
Nb (1)	0	0.201	0	0.003	F (3)	0.360	0.092	0.627	0.015
Nb (2)	0.260	0	0.743	0.003	F (4)	0.125	0.098	0.871	0.015
F (1)	0.148	0	0.450	0.045	F (5)	0.108	0.184	0.300	0.045
F (2)	0.345	0	0.070	0.045	F (6)	0.118	0.282	0.871	0.015

TABLE 2.
Interatomic distances.

(1) Intramolecular					
Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Nb(1)-Nb(1')	5.80 ± 0.006	Nb(2)-F(2)	1.78 ± 0.05	F(4)-F(2)	2.65 ± 0.05
Nb(2)-Nb(2')	5.90 ± 0.006	F(4)-F(4')	2.87 ± 0.03	F(4)-F(5)	2.63 ± 0.05
Nb(1)-F(4)	2.06 ± 0.02	F(4)-F(4')	2.83 ± 0.03	F(4')-F(5)	2.54 ± 0.05
Nb(2)-F(4)	2.07 ± 0.02	F(3)-F(3')	2.66 ± 0.03	F(6)-F(5)	2.62 ± 0.05
Nb(1)-F(6)	1.75 ± 0.02	F(6)-F(6')	2.75 ± 0.03	F(6')-F(5)	2.66 ± 0.05
Nb(1)-F(5)	1.78 ± 0.05	F(4)-F(6)	2.66 ± 0.03	F(3)-F(1)	2.67 ± 0.05
Nb(2)-F(3)	1.78 ± 0.02	F(4)-F(3)	2.70 ± 0.03	F(3)-F(2)	2.62 ± 0.05
Nb(2)-F(1)	1.75 ± 0.05	F(4)-F(1)	2.61 ± 0.05		
(2) Intermolecular					
Bond	Length	Bond	Length	Bond	Length
F(1)-F(4)	3.27 ± 0.05	F(3)-F(6)	3.22 ± 0.03	F(2)-F(2)	3.14 ± 0.07
F(1)-F(4')	3.27 ± 0.05	F(3)-F(3)	3.12 ± 0.03	F(3)-F(6)	3.14 ± 0.03
F(1)-F(5)	2.78 ± 0.07	F(4)-F(5)	3.16 ± 0.05	F(3)-F(6')	3.15 ± 0.03
F(1)-F(1)	2.95 ± 0.07	F(4)-F(6)	3.18 ± 0.03	F(5)-F(5)	3.07 ± 0.07
F(1)-F(2)	2.94 ± 0.07	F(5)-F(3)	3.09 ± 0.05	F(5)-F(5')	3.70 ± 0.07
F(2)-F(3)	3.14 ± 0.05	F(5)-F(3')	3.17 ± 0.05	F(6)-F(6)	2.88 ± 0.003
F(2)-F(3')	3.36 ± 0.05	F(5)-F(6)	3.24 ± 0.05		
F(2)-F(6)	3.18 ± 0.05	F(5)-F(6')	2.89 ± 0.05		
(3) Bond Angles					
F(4)-Nb(1)-F(4')	88.3° ± 1°	F(5)-Nb(1)-F(4)	82.5° ± 2°	F(1)-Nb(2)-F(2)	167° ± 2.5°
F(6)-Nb(1)-F(6')	103.6 ± 1.5	F(5)-Nb(1)-F(4')	86.1 ± 2	F(1)-Nb(2)-F(3)	98.3 ± 2
F(5)-Nb(1)-F(5')	164 ± 2.5	Nb(1)-F(4)-Nb(2)	182.5 ± 2	F(2)-Nb(2)-F(3)	94.8 ± 2
F(5)-Nb(1)-F(6)	95.8 ± 2	F(4)-Nb(2)-F(4')	86.2 ± 1	F(1)-Nb(2)-F(4)	85.5 ± 2
F(5)-Nb(1)-F(6')	97.8 ± 2	F(3)-Nb(2)-F(3')	96.1 ± 1.5	F(2)-Nb(2)-F(4)	86.6 ± 2

DISCUSSION

Niobium and tantalum pentafluorides have the molybdenum pentafluoride structure.⁴ Within experimental error, there are two metal-fluorine bond lengths: (a) 1.77 Å, the distance from the metal to a non-bridging fluorine atom, and (b) 2.06 Å, the distance from the metal to the bridging fluorine atom. Each metal atom is co-ordinated by a distorted octahedron of fluorine atoms, the two environments being the same, within experimental error (Table 2).

The difference in the two bond lengths (0.29 Å), and the shape of the octahedron, are very similar to the dimeric niobium pentachloride,¹³ where the difference in bridging and terminal bond lengths is 0.26 Å, and the co-ordination octahedron is almost identical.

The structure can be regarded as a distorted cubic close-packing of fluorine atoms, with metal atoms occupying one-fifth of the octahedral holes. The close-packing can be seen in Fig. 2, showing the molecular arrangement along [010]. If the fluorine atoms are assumed to be exactly close-packed in the cell, the calculated fluorine-fluorine distance is 2.92 Å. The average distances found are 2.65 Å for intramolecular and 3.14 Å for intermolecular neighbours.

The structure of ruthenium pentafluoride⁵ is based on a hexagonal close-packed arrangement of fluorine atoms, with a tetramer linked by non-linear bridging fluorine atoms. The change in packing from cubic for niobium, tantalum, and molybdenum, to

¹³ Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.

TABLE 3.

Observed and calculated structure factors.

(1) Niobium Pentafluoride																		
<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	
0 0 1	152	172	0 14 4	53	50	$\bar{4}$ 0 4	163	174	0 4 0	171	193	3 17 0	23	29	7 11 0	28	33	
2	157	159				5	53	41		6	138	139			13	<16	14	
4	68	61	0 0 5	<24	26	6	<11	3		19	25	4 0 0	16	32	15	46	48	
6	<20	8	2	45	44					10	228	247	2	13				
8	84	67	4	<23	I	6 0 1	80	49		12	29	35	4	137	139	8 0 0	179	180
10	95	81	6	<22	3	2	105	102		14	84	79	8	148	134	2	<21	2
12	78	71	8	27	41	3	51	64		16	36	49	8	18	16	4	81	72
14	29	25	10	15	24	4	<17	1		18	<12	13	10	90	86	6	51	49
16	<18	1	12	28	34	5	39	40					12	<21	5	8	<20	2
18	17	22				$\bar{5}$ 0 1	146	120	1 1 0	56	54		14	85	68	10	110	106
			0 0 6	<17	2	3	131	148		131	148		16	54	53	12	<16	5
0 0 2	<20	4	2	68	71	2	218	255		126	119					14	40	42
2	167	171	4	23	30	3	60	44		7	85	73						
4	37	35	6	20	26	4	<20	I		9	<17	4	5 1 0	26	23	9 1 0	<21	4
6	72	69				5	55	70		11	50	37	3	96	96	3	83	81
8	125	118	2 0 1	137	129	6	48	53		13	69	65	5	68	68	5	25	20
10	<26	5	2	349	370					15	46	47	7	110	106	7	56	64
12	109	109	3	138	120	8 0 1	112	99		17	26	33	9	20	17	9	<17	12
14	<22	17	4	<22	0	2	<20	6					11	36	26	11	<14	I
16	22	33	5	44	46	3	27	20	2 0 0	<9	12		13	39	43			
			6	63	70	4	72	72		2	237	233	15	27	29	10, 0 0	<20	4
0 0 3	129	116				4	95	92		4	95	92	17	33	42	2	103	97
2	92	73	$\bar{3}$ 0 1	179	182	8 0 1	44	39		6	93	80				4	23	24
4	<24	31	2	34	37	2	<21	2		8	180	184	6 0 0	<17	19	6	25	22
6	40	44	3	45	36	3	93	93		10	<19	7	2	102	115	8	86	72
8	72	66	4	<22	10	4	58	70		12	124	128	4	40	43	10	<11	12
10	65	70	5	69	80	5	<11	0		14	25	37	6	51	51			
12	36	32	6	78	85					16	32	34	8	104	98	11, 1 0	37	41
14	<18	17				10, 0 1	27	28		18	55	61	10	<21	13	3	16	11
16	9	16	4 0 1	129	117	2	95	84		12	93	80	12	93	80	5	69	64
			2	<22	I	3	57	57	3 1 0	60	70		14	21	16	7	14	11
0 0 4	99	105	3	74	80					3	74	69	16	21	24			
2	<26	11	4	109	137	$\bar{1}$ 0, 1	92	84		5	131	133				12, 0 0	62	54
4	109	102	5	55	65	2	62	60		7	94	85	7 1 0	48	53	2	<11	0
6	108	109				3	<14	8		9	79	62	3	19	24	4	44	39
8	<25	9	$\bar{4}$ 0 1	108	70	4	<10	17		11	<20	19	5	95	101			
10	82	85	2	<21	2					13	21	22	7	21	16			
12	<18	3	3	125	113	0 2 0	48	38		15	60	56	9	36	41			

(2) Tantalum Pentafluoride																		
<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	<i>h k l</i>	$ F_o $	F_c	
0 0 1	264	264	$\bar{1}$ 0 4	214	263	$\bar{1}$ 0, 1	150	141	2 10 0	<29	6	5 9 0	<29	19	8 10 0	166	149	
2	<28	5	5	68	60	2	141	117		12	175	203	11	34	28	12	<17	5
3	129	189	6	<14	6	8	<19	18		14	41	55	13	77	71	14	64	55
4	141	207				4	<13	25		16	58	50	15	63	42			
5	46	53	6 0 1	141	90					18	98	81	17	52	55	9 1 0	<27	11
6	<16	2	2	171	205	0 2 0	68	56								3	93	122
			3	120	118	3 1 0	307	312		3	130	113	6 0 0	<28	24	5	36	33
2 0 1	205	204	4	<23	2	6	215	235		3	141	119	2	189	216	7	78	104
2	507	521	5	55	61	8	33	40		5	236	221	4	86	75	9	<20	16
3	235	182				10	308	353		7	147	128	6	81	53	11	<15	5
4	<29	2	$\bar{5}$ 0 1	240	209	12	41	42		9	107	91	8	151	168			
5	92	85	2	375	365	14	126	122		11	20	39	10	<28	15	10, 0 0	<24	10
6	125	121	3	97	69	16	74	76		13	47	47	12	140	125	2	125	130
			4	<27	6	18	<12	17		15	95	83	14	39	26	4	28	34
$\bar{2}$ 0 1	283	285	5	101	119					17	53	39	16	41	32	6	32	32
2	205	195	6	102	95	1 1 0	133	80								8	119	97
3	103	84				3	221	229	4 0 0	160	188	7 1 0	70	89	10	<12	10	
4	<27	13	8 0 1	165	204	5	202	196		2	30	31	3	35	37			
5	121	131	2	<26	9	7	145	132		4	231	232	5	145	165	11, 1 0	38	53
6	152	138	3	41	41	9	28	22		6	225	212	7	35	32	3	13	13
			4	120	124	11	50	45		8	35	26	9	57	66	5	89	89
4 0 1	180	208				13	90	95		10	161	173	11	49	50	7	20	14
2	<28	0	$\bar{3}$ 0 1	94	61	15	81	71		12	<28	5	13	29	33			
3	140	127	2	<28	10	17	62	47		14	114	99	15	74	63	12, 0 0	73	75
4	228	220	3	152	155	2 0 0	<18	11		16	88	72				2	<11	0
5	96	98	4	125	128								8 0 0	199	259	4	40	50
			2	469	460	2	469	460						<29	0			
$\bar{1}$ 0 1	163	125	10, 0 1	49	43	4	162	148	5 1 0	<26	23		4	114	118			
2	<28	6	2	153	138	6	155	132		3	155	169	6	87	95			
3	187	195	3	90	92	8	272	295		5	124	109	8	<26	5			

hexagonal for ruthenium and osmium (see ref. 5), is paralleled by the trifluoride structures¹⁴ and appears to be connected with the element itself, regardless of its valency state.

The pentafluorides of chromium, technetium, and rhenium have recently been shown to have orthorhombic unit cells¹⁵ and a third structure modification seems probable for these elements.

¹⁴ Hepworth, Jack, Peacock, and Westland, *Acta Cryst.*, 1957, **10**, 63.

¹⁵ Edwards, *Proc. Chem. Soc.*, 1963, 205.

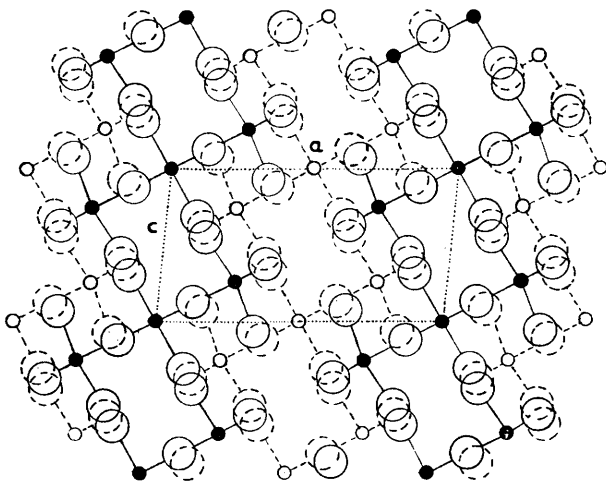


FIG. 2. Projection of the structure along $[010]$ showing the approximate close-packing. Full lines mark the tetramer at $y = 0$, broken lines the tetramer at $y = \frac{1}{2}$; the unit cell is shown dotted.

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