128. *The Crystal Structure of Ruthenium Pentafluoride.*

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The structural unit of solid ruthenium pentafluoride has been determined by *X*-ray single-crystal techniques to be a tetramer with ruthenium atoms at the corners of a rhombus. The metal atoms are linked by non-linear fluorine bridging atoms.

The preparation and some of the properties of ruthenium pentafluoride have been reported by Ruff and Vidic [1] and more recently by Holloway and Peacock.[2] It has been shown that ruthenium pentafluoride can be conveniently prepared in the laboratory by direct fluorination of metallic ruthenium at 300°.[2]

Pure ruthenium pentafluoride is emerald-green and melts at 86·5° to an emerald-green viscous liquid. The dry compound is stable and can be handled and stored in glass at room temperature under rigorously dry conditions.

For the determination of structure, samples were purified and single crystals were set up in evacuated Pyrex glass capillaries as described below.

Experimental

Reaction of Fluorine with Ruthenium.—Elementary fluorine (6 l./hr.), diluted with oxygen-free nitrogen, was passed over ruthenium powder in a nickel vessel at 300°. The product, which contained ruthenium pentafluoride as the major constituent, was collected and sealed under a vacuum. Ruthenium pentafluoride was separated from the impure sample by distillation under a high vacuum.

Growing of Crystals and Filling of Capillaries.—Since ruthenium pentafluoride is hygroscopic it was necessary to seal crystals in Pyrex capillaries under a vacuum. Well-formed crystals grew in evacuated systems at ~40°.

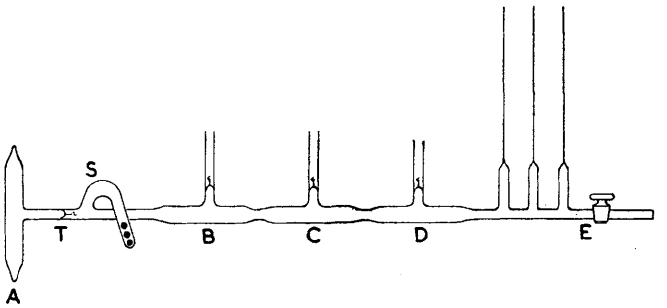

Fig. 1. Apparatus in which single crystals of ruthenium pentafluoride were grown.

The purified sample was held in tube A (Fig. 1). The apparatus was dried by pumping and baking under a vacuum, and was maintained under black vacuum conditions during the experiment. The break-seal, T, was broken with nickel balls. The glass fragments and the nickel balls were returned to the side-arm and sealed off at S. Heating tapes were wound round A and the vessels B, C, and D (1 cm. diameter) and the whole area was heated for about 12 days at 40°. During this time small, well-formed crystals grew in B, C, and D. The sample tubes B and C were sealed off under a vacuum. The tube D was left attached to the capillaries but the tap was removed by sealing at E.

The crystals in D were loosened from the tube walls by judicious cooling with liquid air. A few crystals were manipulated into each of the capillary arms and, by setting up vibrations with a file, individual crystals were transferred to different sections of the capillary tubes. The capillaries were then sealed at suitable points. The crystals were shaken inside the tubes

[1] Ruff and Vidic, *Z. anorg. Chem.*, 1925, **143**, 163.
[2] Holloway and Peacock, *J.*, 1963, 527.

until they became firmly lodged and were set about crystallographic axes by the usual methods.

The tubes B and C were used in conjunction with other sets of capillaries. Glass from the opened break-seals was transferred to a side-arm. The crystals were tapped through the break-seal orifices into the capillaries.

Density.—The density was measured by using a liquid displacement method and a density bottle. The liquid was perfluorofluorene, which does not dissolve or react with ruthenium pentafluoride. The density bottle was filled and stoppered in an atmosphere of dry nitrogen.

Crystal Data.—RuF_5, $M = 197{\cdot}6$, monoclinic, $a = 12{\cdot}47 \pm 0{\cdot}01$, $b = 10{\cdot}01 \pm 0{\cdot}01$, $c = 5{\cdot}42 \pm 0{\cdot}01$ Å, $\beta = 99° 50' \pm 30'$, $V = 667$ Å^3, $D_m = 3{\cdot}82$, $Z = 8$, $D_c = 3{\cdot}92$, $F(000) = 712$. Space group, $P2_{1/a}(C_{2h}^5$ No. 14). CuK_α radiation, single-crystal oscillation and Weissenberg photographs.

The observed systematic absences of reflections were $0k0$ when $k = 2n + 1$ and $h0l$ when $h = 2n + 1$. Values of $h + k$ were both even and odd, but only four $h + k = 2n + 1$ were observed in the $hk0$ zone and these were indexed as 380, 520, 510,0, and 740. The absences indicate unambiguously the space group $P2_{1/a}$.

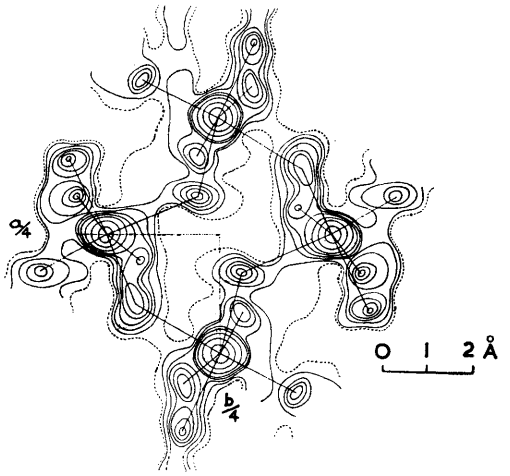

FIG. 2. Electron-density projection along [001]. Contours at 1e/Å^2, except in ruthenium atoms (10e/Å^2).

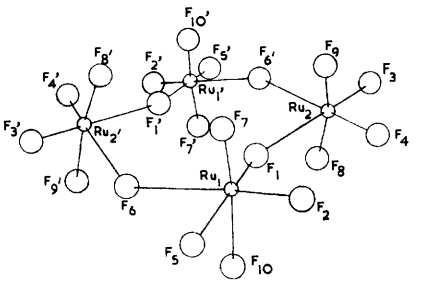

FIG. 3. Tetrameric unit of the ruthenium pentafluoride structure.

Structure Determination.—The linear absorption coefficient was 408 cm.$^{-1}$. The crystals studied had dimensions of 0·19 mm., so that it was necessary to apply absorption corrections. Single crystals were used to obtain intensity data for the $hk0$ and $h0l$ zones. Intensities of the spots were difficult to estimate, as in both zones the spots were extremely small in spite of the fact that fairly large crystals were used. The multiple-film technique was applied and relative intensities were estimated by visual comparison with a standard scale. Values of F^2 were obtained by correction for Lorentz and polarisation factors. 65 of the possible 159 $hk0$ reflections were observed.

The $hk0$ projection was solved first as this promised the best resolution of the atoms. A Patterson synthesis was calculated and interpreted to give the positions of the ruthenium atoms. The phases determined from the ruthenium co-ordinates were used for a Fourier synthesis. The resultant electron-density map did not give complete resolution of all the fluorine atoms, but the positions of five fluorine atoms were determined with certainty. Structure factors were calculated by using the scattering factors of Thomas and Umeda [3] for ruthenium and those tabulated by Berghuis *et al.*[4] for fluorine: values were taken for the un-ionised atoms.[5] At this stage the discrepancy factor, R, was 22%. Difference-synthesis

[3] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[4] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[5] Gutmann and Jack, *Acta Cryst.*, 1951, **4**, 244.

methods were used to place the remaining fluorine atoms, one or two at a time. The discrepancy factor was used as a guide to the refinement produced. R was reduced to 14% and a further cycle gave no co-ordinate shifts. Temperature factors and absorption corrections were introduced at this point. The introduction of an absorption correction of $\mu R = 4{\cdot}7$ allowed the introduction of an overall isotropic temperature factor of $B = 3$ with a slight lowering of R. The least-squares procedure, involving the isotropic temperature factor, led to the different isotropic temperature factors $B_{Ru} = 3{\cdot}0$ and $B_F = 4{\cdot}2$ and the R value fell to 11·8%. The final electron-density projection along [001] is shown in Fig. 2.

The *h0l* projection was solved by the methods outlined above and for these reflections a final R value of 11·2% was obtained (for observed reflections only). In the least-squares

TABLE 1.

Atomic parameters.

Atom	*x/a*	*y/b*	*z/c*	σ (Å)	Atom	*x/a*	*y/b*	*z/c*	σ (Å)
Ru_1	0·000	0·255	0·000	0·001	F_5	0·058	0·083	0·000	0·016
Ru_2	0·199	0·000	0·300	0·001	F_6	0·143	0·350	0·066	0·033
F_1	0·042	0·083	0·206	0·050	F_7	0·040	0·170	0·733	0·045
F_2	0·132	0·333	0·083	0·016	F_8	0·140	0·443	0·600	0·026
F_3	0·183	0·400	0·400	0·050	F_9	0·250	0·083	1·000	0·050
F_4	0·267	0·167	0·500	0·045	F_{10}	0·058	0·175	0·736	0·026

TABLE 2.

Observed and calculated structure factors.

hkl	$\lvert F_o\rvert$	F_c	*hkl*	$\lvert F_o\rvert$	F_c	*hkl*	$\lvert F_o\rvert$	F_c	*hkl*	$\lvert F_o\rvert$	F_c	*hkl*	$\lvert F_o\rvert$	F_c
020	<11	5	10	32	$\bar{21}$	6	<11	3	6	112	137	$\bar{2}00$	25	4
4	146	146	11	7	2	7	<10	12	8	<10	7	1	299	304
6	<12	6	12	50	37	8	<9	9	10	67	81	2	154	163
8	93	101				9	<7	1	12	<9	1	3	<18	41
10	<12	1	510	103	121	10	<6	$\bar{1}$	14	41	39	4	139	135
12	92	73	2	146	$\bar{152}$							5	109	103
			3	117	119	10,10	<12	$\bar{6}$	001	150	167	6	<13	7
			4	12	1	2	<12	$\bar{1}$	2	58	71	7	<6	21
110	38	16	5	92	$\bar{82}$	3	<12	$\bar{3}$	3	203	210			
2	<12	0	6	12	$\bar{4}$	4	127	124	4	124	121	$\bar{4}00$	170	189
3	64	58	7	80	80	5	<11	$\bar{5}$	5	<17	9	1	<18	30
4	<12	5	8	12	$\bar{5}$	6	<10	$\bar{4}$	6	64	45	2	124	113
5	<12	18	9	29	28	7	<8	$\bar{5}$				3	154	162
6	<12	$\bar{7}$	10	17	19	8	73	76	200	25	4	4	<18	35
7	40	47	11	48	42	9	<8	2	1	156	157	5	27	20
8	<12	6	12	4	1	10	<3	3	2	55	81	6	113	102
9	<11	5							3	47	55	7	<5	23
10	<9	8	610	<12	$\bar{8}$	11,10	<12	19	4	<18	15			
11	20	24	2	67	$\bar{61}$	2	<11	$\bar{3}$	5	128	87	$\bar{6}00$	143	134
12	<6	$\bar{2}$	3	<12	$\bar{4}$	3	<11	28				1	150	146
			4	121	121	4	<11	2	400	170	189	2	<18	$\bar{25}$
			5	<12	3	5	<10	16	1	198	224	3	70	48
210	<11	$\bar{15}$	6	47	$\bar{44}$	6	<9	$\bar{2}$	2	<17	$\bar{1}$	4	79	64
2	290	$\bar{280}$	7	<12	7	7	20	19	3	49	54	5	<16	22
3	<12	$\bar{45}$	8	66	77	8	<6	$\bar{5}$	4	169	168	6	<15	1
4	39	28	9	<10	$\bar{1}$	9	<4	0	5	56	65			
5	<12	$\bar{21}$	10	19	$\bar{24}$							$\bar{8}00$	<18	15
6	156	$\bar{159}$	11	<6	$\bar{2}$	12,10	<11	$\bar{12}$	600	143	134	1	51	54
7	<12	$\bar{1}$				2	65	$\bar{77}$	1	<7	$\bar{3}$	2	220	234
8	<12	12	710	70	$\bar{71}$	3	<10	$\bar{5}$	2	105	112	3	49	51
9	<11	$\bar{5}$	2	<12	$\bar{8}$	4	<10	12	3	107	124	4	<17	9
10	63	$\bar{74}$	3	58	$\bar{85}$	5	<9	$\bar{7}$	4	<16	$\bar{5}$	5	62	64
11	<8	0	4	32	$\bar{12}$	6	74	$\bar{66}$	5	49	57	6	43	49
12	<6	$\bar{5}$	5	61	$\bar{68}$	7	<6	0	6	41	42			
			6	<11	$\bar{7}$	8	<5	8				$\bar{10}$,00	75	85
			7	19	$\bar{18}$				800	<18	15	1	47	45
310	116	$\bar{69}$	8	<8	$\bar{5}$	13,10	29	$\bar{35}$	1	165	170	2	<18	28
2	<12	$\bar{1}$	9	44	$\bar{12}$	2	<9	$\bar{2}$	2	107	99	3	116	107
3	92	$\bar{102}$	10	<7	$\bar{4}$	3	25	$\bar{25}$	3	<17	$\bar{12}$	4	43	50
4	<12	$\bar{7}$	11	21	$\bar{10}$	4	<8	$\bar{0}$	4	60	52	5	<6	3
5	102	$\bar{102}$				5	39	$\bar{40}$	5	<8	1	6	21	42
6	<12	0	810	<12	$\bar{18}$	6	<6	$\bar{1}$						
7	55	$\bar{57}$	2	118	$\bar{154}$				10,00	75	85	$\bar{12}$,00	<16	0
8	25	$\bar{11}$	3	<12	$\bar{12}$	14,10	<8	3	1	45	39	1	66	92
9	61	$\bar{60}$	4	<12	13	2	18	$\bar{26}$	2	<16	0	2	54	71
10	<10	$\bar{2}$	5	<12	$\bar{2}$	3	<7	1	3	60	66	3	<15	1
11	<8	$\bar{12}$	6	74	$\bar{84}$	4	38	$\bar{37}$	4	<10	33	4	43	43
12	<5	$\bar{4}$	7	<11	6	5	<5	$\bar{2}$				5	56	42
			8	<10	4				12,00	<16	0			
410	12	9	9	<8	4	15,10	34	22	1	<15	19	$\bar{11}$,00	41	45
2	80	$\bar{90}$	10	60	$\bar{65}$	2	<5	6	2	77	83	1	<12	3
3	12	$\bar{32}$	11	<5	3	3	34	27	3	<10	27	2	36	47
4	139	132				4	<4	1				3	36	41
5	12	12	910	29	18				14,00	41	45	4	<9	3
6	66	$\bar{71}$	2	<12	7	16,10	<3	0	1	60	54			
7	12	$\bar{9}$	3	26	31				2	<8	12	$\bar{16}$,00	21	39
8	79	17	4	<12	$\bar{3}$	200	38	35				1	51	50
9	11	$\bar{6}$	5	<12	1	4	175	184	16,00	21	39	2	<6	1

procedure the isotropic temperature factors were $B_{Ru} = 2{\cdot}7$ and $B_F = 4{\cdot}0$. The absorption correction, μR, was given the value 4·7.

Weissenberg photographs of the $0kl$ zone were also obtained. The spots were again small and exceedingly difficult to estimate, and they were not used in the determination.

The final atomic parameters, with their estimated standard deviations (σ) are given in Table 1 and observed and calculated structure factors are shown in Table 2.

Description of the Structure.—Ruthenium pentafluoride possesses a distorted version of the molybdenum pentafluoride structure [6] (Table 3, Fig. 3). In the tetrameric unit Ru_4F_{20} the ruthenium atoms are at the corners of a rhombus with non-linear Ru–F–Ru bonds. The arrangement of fluorine atoms around each ruthenium atom forms a distorted octahedron. The ruthenium pentafluoride bond lengths can be divided into three groups: (*a*) about 1·83 Å,

TABLE 3.

Interatomic distances in ruthenium pentafluoride.

(1) Intramolecular

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
Ru_2–Ru_2	5·45 ± 0·002	Ru_2–F_8	1·98 ± 0·03	F_3–F_8	2·63 ± 0·15	F_6–F_5	2·87 ± 0·04
Ru_1–Ru_1	5·11 ± 0·002	Ru_2–F_9	2·02 ± 0·1	F_2–F_{10}	2·72 ± 0·04	F_1–F_7	2·75 ± 0·14
Ru_2–F_1	2·10 ± 0·1	Ru_1–F_7	1·82 ± 0·1	F_4–F_8	2·85 ± 0·07	F_1–F_{10}	2·72 ± 0·10
Ru_2–F_6	2·01 ± 0·03	Ru_1–F_{10}	1·78 ± 0·03	F_5–F_7	2·89 ± 0·10	F_1–F_2	2·86 ± 0·10
Ru_1–F_1	2·07 ± 0·1			F_3–F_9	2·85 ± 0·17	F_1–F_6	2·81 ± 0·10
Ru_1–F_6	2·00 ± 0·03	F_2–F_4	2·91 ± 0·06	F_2–F_7	2·88 ± 0·10	F_1–F_9	2·99 ± 0·14
Ru_2–F_3	1·79 ± 0·15	F_5–F_2	2·48 ± 0·03	F_4–F_9	2·81 ± 0·11	F_1–F_8	2·67 ± 0·10
Ru_2–F_4	2·09 ± 0·06	F_4–F_3	2·83 ± 0·15	F_9–F_6	2·74 ± 0·10	F_1–F_4	3·09 ± 0·11
Ru_1–F_2	1·94 ± 0·02	F_5–F_{10}	2·81 ± 0·04	F_8–F_6	2·64 ± 0·04	F_1–F_6	2·82 ± 0·10
Ru_1–F_5	1·78 ± 0·02	F_6–F_{10}	2·76 ± 0·08				

(2) Intermolecular

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
F_4–$F_{6'}$	2·85 ± 0·06	$F_{8'}$–F_7	3·04 ± 0·10	F_{10}–F_8	3·49 ± 0·04	$F_{10'}$–F_7	3·66 ± 0·10
F_4–F_5	3·85 ± 0·06	F_7–F_8	3·04 ± 0·10	F_9–F_8	2·74 ± 0·10	$F_{9'}$–F_8	2·74 ± 0·10
F_2–F_3	2·84 ± 0·15						

(3) Bond angles

Bond	Angle	Bond	Angle	Bond	Angle
Ru_1–F_1–Ru_2	127° 12′ ± 2°	F_5–Ru_1–F_2	83° 21′ ± 1°	F_3–Ru_2–F_9	96° 40′ ± 8°
Ru_2–F_6–Ru_1	136° 43′ ± 2°	F_{10}–Ru_1–F_1	89° 37′ ± 1°	F_1–Ru_2–F_4	96° 21′ ± 4°
F_6–Ru_1–F_1	87° 22′ ± 2·5°	F_1–Ru_1–F_7	89° 46′ ± 2°	F_4–Ru_2–F_3	94° 27′ ± 7°
F_1–Ru_2–$F_{6'}$	86° 52′ ± 2·5°	F_{10}–Ru_1–F_2	93° 54′ ± 5°	F_4–Ru_2–F_8	88° 54′ ± 3°
		F_2–Ru_1–F_7	100° 10′ ± 5°	F_8–Ru_2–F_6	82° 48′ ± 1°
F_6–Ru_1–F_{10}	93° 38′ ± 2°	F_1–Ru_2–F_8	81° 36′ ± 5·5°	$F_{6'}$–Ru_2–F_9	85° 37′ ± 4·5°
F_6–Ru_1–F_5	98° 38′ ± 2°	F_8–Ru_2–F_3	88° 23′ ± 7°		
F_5–Ru_1–F_{10}	104° 9′ ± 2°				

the distance of the singly bonded fluorines to Ru_1, (*b*) about 1·97 Å, the distance of the singly bonded fluorines to Ru_2, and (*c*) about 2·05 Å, the distance of the ruthenium atoms to the doubly bonded fluorine atoms.

DISCUSSION

The average of the ruthenium–fluoride distances (*a*) and (*b*) is 1·90 Å and both are shorter than the sum of either the covalent (2·00 Å) or the ionic (2·08 Å) radii of the atoms. The long bond (*c*) is between the theoretical values and reflects the different environments of the bridging fluorine atoms. The octahedral arrangement about the ruthenium metal atoms is much the same as in MoF_5, but the fluorine bridges are not linear.

An interesting, but as yet unexplained, feature of both the RuF_5 and the MoF_5 structure is that the " out-of-plane " or " up/down " fluorine atoms in each tetramer appear to be drawn towards the centre of the tetramer.[6] The effect is clearly shown in Fig. 2. The same effect also occurs in molybdenum pentachloride,[7] niobium pentachloride,[8] and niobium tetraiodide.[9]

[6] Edwards, Peacock, and Small, *J.*, 1962, 4486.
[7] Sands and Zalkin, *Acta Cryst.*, 1959, **12**, 723.
[8] Zalkin and Sands, *Acta Cryst.*, 1958, **11**, 615.
[9] Dahl and Wampler, *Acta Cryst.*, 1962, **15**, 903.

It is interesting that similar ring forms with non-linear fluorine bridges occur in both ruthenium pentafluoride and ruthenium trifluoride.[10] Ruthenium trifluoride has a distorted hexagonal close-packed structure and each fluorine atom occupies a volume of about 16·4 Å^3. If the fluorine atoms in the pentafluoride are of the same volume, then the expected cell volume for RuF_5 is 656 Å^3, only 11 Å less than the actual value. It is concluded that ruthenium pentafluoride has a similar close-packed structure.

The transition-metal pentafluorides of the second and third periods are a homogeneous group of compounds with similar melting and boiling points, and these point to structural similarities.

Single-crystal studies in these laboratories have confirmed the close similarity of niobium and tantalum pentafluoride to molybdenum pentafluoride.[11] The powder pattern of osmium pentafluoride indicates that this is isostructural with ruthenium pentafluoride.[12] Preliminary *X*-ray, powder and single-crystal studies of the pentafluorides of chromium, technetium, and rhenium have shown that they have orthorhombic unit cells which are evidently of a third structure type.[11]

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Department of Chemistry, The University,
Edgbaston, Birmingham 15. [*Received, July 20th,* 1963.]

[10] Hepworth, Jack, Peacock, and Westland, *Acta Cryst.*, 1957, **10**, 63.
[11] Edwards, unpublished work.
[12] Holloway, unpublished observation.