The Crystal Structures of the Trifluorides of Iron, Cobalt, Ruthenium, Rhodium, Palladium and Iridium

By M. A. Hepworth, K. H. Jack, R. D. Peacock* and G. J. Westland

Chemistry Department, King's College, Newcastle-on-Tyne, England

The structures of FeF_3, CoF_3, RuF_3, RhF_3, PdF_3, and IrF_3 are rhombohedral with atoms in the following special positions of space group $R\bar{3}c$: 2M at 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and 6F at $\pm(x, \frac{1}{2}-x, \frac{1}{4})$; $\pm(\frac{1}{2}-x, \frac{1}{4}, x)$; $\pm(\frac{1}{4}, x, \frac{1}{2}-x)$. For IrF_3, PdF_3 and RhF_3, $x = -0.083 \pm 0.003$; i.e., $x = -\frac{1}{12}$ within experimental error. For RuF_3, $x = -0.100 \pm 0.005$; for CoF_3, $x = -0.15 \pm 0.01$; and for FeF_3 $x = -0.164 \pm 0.003$. In each case, direct experimental evidence shows that the structural unit is not the unimolecular rhombohedron proposed for some of these trifluorides by earlier workers. Regular or almost regular octahedra of fluorine atoms, each with a metal atom at its centre, are joined by sharing corners only. The fluorine-atom arrangement is hexagonal close-packed in RhF_3, PdF_3 and IrF_3; for the other three trifluorides the distortion from hexagonal close-packing increases in the order RuF_3, CoF_3, FeF_3. Relationships between the different structures typified by MoF_3, VF_3 and PdF_3 respectively, are discussed.

RuF_3, and to a smaller extent IrF_3, both show variabilities in their unit-cell dimensions which, it is claimed, are due to variations from the stoichiometric composition caused by the presence in the lattice of cations with valencies other than three.

Introduction

Trifluoride structures previously reported from this laboratory (Gutmann & Jack, 1951; Jack & Gutmann, 1951) are of two types. MoF_3 and TaF_3 are isostructural with ReO_3 and have a cubic close-packed arrangement of fluorine atoms in which one-fourth of the octahedral interstices are occupied by metal atoms and where one-fourth of the fluorine-atom sites remain vacant. VF_3 resembles MoF_3 in that almost regular MF_6 octahedra are joined by sharing corners, but it represents a separate trifluoride type since its fluorine-atom arrangement is considerably distorted from a hexagonal close-packing. The rhombohedral unit cell contains V_2F_6, i.e. it is 'bimolecular'. The only structures of transition-element trifluorides which had previously been investigated were those of ScF_3, FeF_3, CoF_3, RhF_3 and PdF_3. ScF_3 was claimed to have a rhombohedrally distorted ReO_3 structure with a unimolecular cell (Nowacki, 1939). Some workers (Wooster, 1933; Nowacki, 1939) considered FeF_3, CoF_3, RhF_3 and PdF_3 also to belong to this structure-type, but others (Ebert, 1931; Ketelaar, 1933) claimed that they were similar to AlF_3 with a bimolecular cell, although all the observed reflexions were indexed on a rhombohedral unit containing only one molecule. The need for a further study of these compounds (see Wyckoff, 1948, § 1, chap. 5, text p. 13) was emphasized by the results obtained for VF_3 (Jack & Gutmann, 1951). Ehrlich & Pietzka (1954) have shown that TiF_3 is probably isostructural with VF_3, although

a complete structural analysis was not attempted*; NbF_3 is isostructural with MoF_3 and TaF_3 (Ehrlich, Plöger & Pietzka, 1955).

In the present paper, quantitative X-ray investigations of the trifluorides of Fe, Co, Ru, Rh, Pd and Ir are described. The results, together with those previously reported, offer a basis for classifying trifluorides into three types depending upon their fluorine-atom arrangements. For FeF_3, CoF_3, RhF_3 and PdF_3, where doubts had hitherto existed, direct evidence obtained by the use of crystal-reflected monochromatic X-radiation shows that the rhombohedral unit cells are bimolecular.

Experimental

CoF_3 was prepared by the action of anhydrous fluorine on finely powdered $CoCl_2$ at about 250° C. and FeF_3 was obtained by direct fluorination of electrolytic iron powder at 500° C. RhF_3 and PdF_3 were prepared by the reactions of dry fluorine on RhI_3 and on PdI_2 (palladous iodide), respectively, at about 400° C.

Specimens used for the structure determination of RuF_3 were prepared by reacting ruthenium pentafluoride, RuF_5, with excess of iodine at about 150° C. (Aynsley, Peacock & Robinson, 1952). The pentafluoride was reduced to the non-volatile trifluoride

$$5\,RuF_5 + I_2 \rightarrow 5\,RuF_3 + 2\,IF_5$$
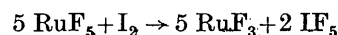
which was then heated at 500° C. for 12 hr. to allow

---

* Now at Department of Chemistry, Imperial College of Science and Technology, London S.W. 7, England.

---

crystal growth and to ensure the complete removal of possible traces of iodine, iodine pentafluoride, and unchanged ruthenium pentafluoride. It was noticed that different preparations of RuF_3 showed small but unmistakable differences in their unit-cell dimensions. Although no elements other than ruthenium and fluorine were detected qualitatively in the different specimens, the limits of error in the quantitative analyses were too large to allow any precise correlation between composition and unit-cell size (found: Ru 64·2–65·1±0·6%, F 34·3–35·5±1·0%; calculated for RuF_3: Ru 64·4%, F 35·6%). Further experiments showed that the variation in cell size is associated with the relative proportions of iodine and ruthenium pentafluoride used in the preparation. With an excess of RuF_5, the unit-cell volume is a minimum. If, instead of iodine, sulphur is used as a reducing agent, the unit-cell dimensions of the product obtained by reduction of RuF_5 with a large excess of sulphur are identical with those obtained by using a large excess of iodine. Since these dimensions are at the upper limit of the observed range of values, it is considered, as shown below, that they represent the 'ideal' RuF_3 composition. Other specimens with smaller cell sizes probably have defect structures.

A similar but smaller variation in unit-cell dimensions was found in different specimens of IrF_3. These were prepared by two methods. The first, by heating iridium metal powder in a mixed stream of nitrogen and iridium hexafluoride vapour at 500° C.,

$$Ir + IrF_6 \rightarrow 2\,IrF_3\,,$$
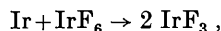
produced a well-crystalline trifluoride together with some unchanged metal. The second method, the thermal decomposition at 400–450° C. of iridium tetrafluoride, IrF_4, gave pure but poorly-crystalline IrF_3 (found: Ir 77·0%; calculated: Ir 77·3%). X-ray intensities were therefore obtained from photographs of the material which contained iridium impurity, since reflexions from the metal and from the trifluoride did not overlap and since the trifluoride diffraction pattern

was identical with, but sharper than that of the homogeneous specimen.

Because most transition-element trifluorides are hydrolysed in moist air, thin-walled X-ray-specimen capillaries, 0·5 mm. diameter (supplied by Pantak Ltd, Slough) were filled and sealed off in a dry box.

X-ray powder photographs were taken at 18±2° C. with crystal-reflected radiation from a lithium fluoride monochromator. Either Fe $K\alpha$ radiation (α_1, 1·93597; α_2, 1·93991 Å) or Co $K\alpha$ radiation (α_1, 1·78890; α_2, 1·79279 Å) were used with a 19 cm. (or in the case of CoF_3 a 9 cm.) Unicam camera. For every structure determination, duplicate films were microphotometered with a Dobson-type instrument built from a design by Taylor (1951), and values of the integrated intensities in arbitrary units were obtained by measuring areas under the plotted photometer curves with a planimeter.

Results

The observed X-ray reflexions from each of the trifluorides were indexed on a bimolecular rhombohedral unit cell the dimensions of which are listed in Table 1. The dimensions of the unimolecular rhombohedral pseudo-cells and of the corresponding hexagonal cells are also included in this table in order to allow comparison with some of the claims of previous workers.

Agreement between the observed and calculated intensities was obtained for the six trifluorides (see Table 2) by placing the atoms in the following positions of space group $R\bar{3}c$ (*International Tables*, 1952, No. 167):

$$2\,M \text{ in } (b) \text{ at } 0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2},$$
$$6\,F \text{ in } (e) \text{ at } \pm(x,\tfrac{1}{2}-x,\tfrac{1}{4});\ \pm(\tfrac{1}{2}-x,\tfrac{1}{4},x);$$
$$\pm(\tfrac{1}{4},x,\tfrac{1}{2}-x).$$

Values of x are

$$-0·164\pm0·003 \text{ for } FeF_3,$$
$$-0·15\ \pm0·01\ \text{ for } CoF_3,$$
$$-0·100\pm0·005 \text{ for } RuF_3,$$
$$-0·083\pm0·003 \text{ for } RhF_3,\ PdF_3 \text{ and } IrF_3.$$

Table 1. *Cell dimensions of* FeF_3, CoF_3, RuF_3, RhF_3, PdF_3 and IrF_3

(Dimensions of the true structural units are given in bold figures)

	Unimolecular rhombohedron		Bimolecular rhombohedron		Hexagonal pseudo-cell		
	a (Å)	α (°)	a (Å)	α (°)	a (Å)	c (Å)	Author
FeF_3	3·734	88·22	**5·362±0·001**	**57·99±0·01**	5·198	13·331	Present work
	3·764	88·24	5·372	58·04	5·212	13·35	Ebert (1931)
CoF_3	3·648	87·29	**5·279±0·002**	**56·97±0·02**	5·035	13·218	Present work
	3·671	87·33	5·310	57·04	5·071	13·29	Ebert (1931)
RuF_3*	3·672	85·13	**5·408±0·001**	**54·67±0·01**	4·967	13·756	Present work
RhF_3	3·611	84·89	**5·330±0·001**	**54·42±0·01**	4·874	13·579	Present work
	3·624	84·80	5·354	54·32	4·888	13·65	Ebert (1931)
PdF_3	3·728	84·40	**5·5234±0·0005**	**53·925±0·005**	5·009	14·118	Present work
	3·760	84·65	5·560	54·17	5·063	14·19	Ebert (1931)
IrF_3*	3·666	84·72	**5·418±0·002**	**54·13±0·03**	4·940	13·819	Present work

* See also Table 6.

The estimated limits of error for the fluorine parameters and for the cell dimensions are larger for CoF_3 than for the other five trifluorides because the cobalt salt was less crystalline and gave diffuse reflexions at higher Bragg angles.

In Table 2 the reflexions marked with an asterisk have $h+k+l$ odd and therefore cannot be accounted for by a unimolecular rhombohedron; they were unobserved or incorrectly indexed for the fluorides studied in previous work (Ebert, 1931). The structure amplitudes of such reflexions are dependent solely upon the fluorine-atom arrangement and they may be termed for convenience 'fluorine-only' reflexions. For FeF_3 and CoF_3 all possible reflexions were observed except for the systematic absences required by space group $R\bar{3}c$, i.e. hhl where l is odd. For RhF_3, PdF_3 and IrF_3 there were additional absences. The only 'fluorine-only' reflexions observed (i.e. when $h+k+l = 2n+1$) were those for which $h+k+l = 3(2n+1)$, namely with indices 210, 432, 31$\bar{1}$ and 531. This restriction indicated that the fluorine-atom arrangement was close to, if not exactly, close-packed hexagonal. Trial-and-error methods gave best agreement between the observed and calculated intensities for all

Table 2. *Calculated and observed X-ray intensities for* FeF_3, CoF_3, RuF_3, RhF_3, PdF_3 *and* IrF_3

(Fe $K\alpha$ or Co $K\alpha$ radiation; the reflexions are listed in order of their increasing Bragg angles)

	FeF₃			CoF₃			RuF₃	
hkl	I_c	I_o	*hkl*	I_c	I_o	*hkl*	I_c	I_o
110	211	210	110	168	175	110	58	59
211	31	31	211	27	27	211	38	35
10$\bar{1}$	15	16	10$\bar{1}$	11	11	10$\bar{1}$	18	18
†*210	40	42	222	< 0·1 } 28	26	222	2	3
222	0·2	0	†*210	28		†*201	14	14
200	3	3	200	4	5	200	25	24
220	71	67	220	32	32	220	29	32
321	79 } 88	84	321	32	41	321	70	67
*20$\bar{1}$	9		*20$\bar{1}$	3	3	*20$\bar{1}$	0·2	0
21$\bar{1}$	46	45	21$\bar{1}$	18	15	332	20 } 62	61
332	9	10	332	4	5	21$\bar{1}$	42	
310	24	25	310	11	12	310	39	37
2$\bar{1}\bar{1}$	27	28	2$\bar{1}\bar{1}$	13	12	2$\bar{1}\bar{1}$	38	36
*320	5	5	*320	2	vw	*320	0·2	0
422	29	27	422	8	8	422	19	19
20$\bar{2}$	13	13	†*432	3 } 11	11	433	18 } 24	25
†*432	8	8	433	5		†*432	6	
433	15	16	20$\bar{2}$	3		*421	0·2	0
*421	4	4	*421	1	0	20$\bar{2}$	10	10
†*31$\bar{1}$	2		411	1		330	6 } 12	13
411	4 } 20	21	330	1 } 3	vw	411	6	
330	4		†*31$\bar{1}$	1		†*31$\bar{1}$	4	4
*21$\bar{2}$	10		*21$\bar{2}$	2	vw	*21$\bar{2}$	< 0·1	0
30$\bar{1}$	38	36	30$\bar{1}$	10	mw	431	33 } 69	67
431	15	14	431	4	w	30$\bar{1}$	36	
32$\bar{1}$	6	5	32$\bar{1}$	2	vw	442	15	16
442	2	2	442	1	0	444	11	11
*410	9	8	444	2 } 4	w	32$\bar{1}$	29	28
420	14	15	*410	2		*410	< 0·1 } 48	46
444	11 } 21	19	420	4	w	420	48	
22$\bar{2}$	10		22$\bar{2}$	3	vw	22$\bar{2}$	20	20
400	9	8	400	1	0	532	35	38
532	23	21	532	4	w	543	24	27
*430	9	8	*430	1	0	400	16	16
*30$\bar{2}$	0·1	0	543	1	0	*430	< 0·1	0
543	9 } 16	16	*30$\bar{2}$	0	0	*542	0·1	0
31$\bar{2}$	7		31$\bar{2}$	1	0	*302	0·1	0
521	8	10	521	1 } 1	vw	521	40 } 79	79
*542	6 } 75	68	*542	0·1		31$\bar{2}$	39	
41$\bar{1}$	69		41$\bar{1}$	7 } 7	w	†*531	5	5
3$\bar{2}\bar{1}$	27	29	†*531	0·4		554	28	30
†*531	4	5				41$\bar{1}$	66	61
						3$\bar{2}\bar{1}$	43	42
						*42$\bar{1}$	0·1	0
						†*40$\bar{1}$	6 } 12	12
						†*32$\bar{2}$	6	
						440	44	44
						541	186	185

* 'Fluorine-only' reflexions requiring a bimolecular unit cell.
† 'Fluorine-only' reflexions for which $h+k+l = 3(2n+1)$.

Table 2 (cont.)

RhF₃

hkl	I_c	I_o
110	206	208
211	164	156
$10\bar{1}$	80	73
222	10	10
†*210	53	61
200	125	121
220	114	121
321	321	325
332	102 ⎱ 302	314
$21\bar{1}$	200 ⎰	
310	191	196
$2\bar{1}\bar{1}$	195	190
422	94	99
433	94	105
†*$43\bar{2}$	26	26
$20\bar{2}$	61	53
330	35 ⎱ 70	70
411	35 ⎰	
†*$31\bar{1}$	25	30
431	210	222
$30\bar{1}$	213	216
442	109	100
444	72	71
$32\bar{1}$	238	213
420	384	356
$22\bar{2}$	160	171
532	340	337
543	239	250
400	222	s

PdF₃

hkl	I_c	I_o
110	146	148
211	115	109
$10\bar{1}$	56	57
222	7	8
†*210	35	39
200	84	83
220	76	78
321	214	202
332	67	64
$21\bar{1}$	131	129
310	124	123
$2\bar{1}\bar{1}$	124	122
422	59	58
433	58	58
†*$43\bar{2}$	15	15
$20\bar{2}$	37	42
330	21 ⎱ 42	49
411	21 ⎰	
†*$31\bar{1}$	14	14
431	121	123
$30\bar{1}$	122 ⎱ 184	191
442	62 ⎰	
444	40	39
$32\bar{1}$	132	120
420	201	189
$22\bar{2}$	80 ⎱	
532	160 ⎰ 349	355
543	109 ⎰	
400	96	76
521	312	s
312	387	s
554	214	ms
†*531	50	w

IrF₃

hkl	I_c	I_o
110	395	403
211	278	280
$10\bar{1}$	186	184
222	40	41
†*210	27	28
200	211	205
220	187	186
321	440	441
332	167	167
$21\bar{1}$	328	332
310	311	289
$2\bar{1}\bar{1}$	231	226
422	149	150
433	149	153
†*$43\bar{2}$	11	7
$20\bar{2}$	120	120
330	95 ⎱ 190	192
411	95 ⎰	
†*$31\bar{1}$	10	7
431	314	347
$30\bar{1}$	317	340
442	162	mw
444	79	w
$32\bar{1}$	347	334
420	459	446
$22\bar{2}$	217 ⎱	
532	444 ⎰ 1041	1144
543	380 ⎰	
400	274	m
521	1242	vs

the reflexions of RhF₃, PdF₃ and IrF₃ with $x = -0\cdot083\pm0\cdot003$, i.e., within the small limits of experimental error, $x = -\frac{1}{12}$. For RuF₃, again only the 210, 432, $31\bar{1}$ and 531 'fluorine-only' reflexions were observed but the value of $x = -\frac{1}{12}$, which is required for a perfect hexagonal close-packing of the fluorine atoms, did not give sufficiently good agreement between the observed and calculated intensities of the strong reflexions. The final parameter, $x = -0\cdot100\pm0\cdot005$, obtained by trial-and-error refinement, is well outside the limits of error for a close-packed hexagonal arrangement of fluorine atoms.

Discussion

FeF₃ and CoF₃ are isostructural with vanadium trifluoride, VF₃. This structure type, which has previously been described and represented diagrammatically (see Jack & Gutmann, 1951), consists of alternate and regularly spaced planes of metal atoms and planes of fluorine atoms perpendicular to the [111] direction. Each fluorine atom has four nearest fluorine neighbours in its own plane (distance p) and four others in adjacent fluorine planes (two in the plane above and two below; distance q). Each metal atom is equidistant (distance r) from six fluorine atoms which form an almost regular octahedron round it.

The MF_6 co-ordination octahedra are joined by sharing all corners, and in conformity with the electrostatic valence rule (see Pauling, 1940) each fluorine therefore has two metal-atom ligands. The M–F–M bond angle (φ) differs considerably from 180°. The metal atoms form a rhombohedrally-distorted simple cubic lattice in which each is equidistant from six neighbours (distance s). The arrangement of fluorine atoms in VF₃, FeF₃ and CoF₃ may be regarded as a considerably distorted hexagonal close-packing, each atom being displaced by the same amount (distance t) from a close-packed hexagonal site. Alternatively, these structures are distortions of the cubic MoF₃ and TaF₃ types with their fluorine atoms displaced (each by a distance u) from a cubic close-packing.

Contrary to suggestions made by previous workers, RhF₃ and PdF₃ are not isostructural with FeF₃ and CoF₃. The two former trifluorides, and also IrF₃, have a close-packed hexagonal fluorine-atom arrangement. Successive close-packed planes are slightly compressed along the trigonal axis so that the axial ratios (1·608, 1·627, and 1·619 respectively for RhF₃, PdF₃, and IrF₃) are less than the ideal value of 1·633. Each fluorine atom thus has six equidistant fluorine neighbours in its own plane (distance p; cf. FeF₃ and CoF₃) and six others at a slightly shorter distance (q) in adjacent planes (three above and three below). The

Table 3. *Structural data for trifluorides classified according to type*

(Co-ordination numbers are given in parentheses)

Type		Interatomic distances (Å)				Bond angle (°) M–F–M φ	Displacements (Å)		F-atom parameter x
		F–F p	F–F q	M–F r	M–M s		from h.c.p. t	from c.c.p. u	
MoF$_3$	NbF$_3$	(4) 2·76	(4) 2·76	(6) 1·95	(6) 3·90	180	0·92	0	−0·250
	MoF$_3$	(4) 2·76	(4) 2·76	(6) 1·95	(6) 3·90	180	0·92	0	−0·250
	TaF$_3$	(4) 2·76	(4) 2·76	(6) 1·95	(6) 3·90	180	0·92	0	−0·250
VF$_3$	VF$_3$	(4) 2·75	(4) 2·74	(6) 1·94	(6) 3·73	147	0·32	0·54	−0·145
	FeF$_3$	(4) 2·72	(4) 2·72	(6) 1·92	(6) 3·73	153	0·42	0·45	−0·164
	CoF$_3$	(4) 2·66	(4) 2·69	(6) 1·89	(6) 3·65	149	0·34	0·50	−0·15
	RuF$_3$	(4) 2·80	(4) 2·81	(6) 1·98	(6) 3·37	136	0·08	0·75	−0·100
PdF$_3$	RhF$_3$	(6) 2·81	(6) 2·79	(6) 1·98	(6) 3·61	132	0	0·81	−0·083
	PdF$_3$	(6) 2·89	(6) 2·89	(6) 2·04	(6) 3·73	132	0	0·84	−0·083
	IrF$_3$	(6) 2·83	(6) 2·83	(6) 2·01	(6) 3·67	132	0	0·82	−0·083

metal atoms occupy in an ordered manner one-third of the number of octahedral interstices in this close-packing of fluorine atoms.

RuF$_3$ must be classed with VF$_3$, FeF$_3$ and CoF$_3$, since its fluorine-atom arrangement is distorted from close-packed hexagonal. The displacement (t) of each fluorine atom from a close-packed hexagonal site is only 0·08 Å while the corresponding displacement (u) from cubic close-packing is 0·75 Å.

In Table 3 the distances p, q, r, s, t and u, and the angles φ are compared for the fluorides NbF$_3$, MoF$_3$, TaF$_3$, VF$_3$, FeF$_3$, CoF$_3$, RuF$_3$, RhF$_3$, PdF$_3$ and IrF$_3$. It is immediately evident that VF$_3$, FeF$_3$ and CoF$_3$ are structurally about mid-way between the MoF$_3$ and PdF$_3$ types. This is also apparent when the fluorine parameters, all referred to space group $R\bar{3}c$, are compared (see Table 3 also). It is concluded that the trifluorides may be classified into three groups:

(i) Typified by MoF$_3$ and TaF$_3$; the fluorine-atom arrangement is cubic close-packed with the corner site of each face-centred cube left vacant (see Gutmann & Jack, 1951).

(ii) The fluorines are hexagonal close-packed, e.g. RhF$_3$, PdF$_3$ and IrF$_3$.

(iii) The arrangement of fluorine atoms is inter-mediate between the arrangements of types (i) and (ii), e.g. VF$_3$, FeF$_3$, CoF$_3$. RuF$_3$ must also be included in this group although its structural distortion from type (ii) is small.

Fig. 1(a) illustrates the type (iii) structure. The bimolecular rhombohedral cell contains the equivalent of two unimolecular pseudo-cubes with metal atoms at the corners and with the fluorine atoms displaced from the mid-points of the pseudo-cell edges. These displacements are in opposite senses in adjacent uni-molecular cells, so that the true rhombohedral unit contains M_2F_6. Fig. 1(b) shows one of the pseudo-cells, and in Fig. 1(c) the type (i) structure (e.g. MoF$_3$) is depicted in the same orientation for com-parison.
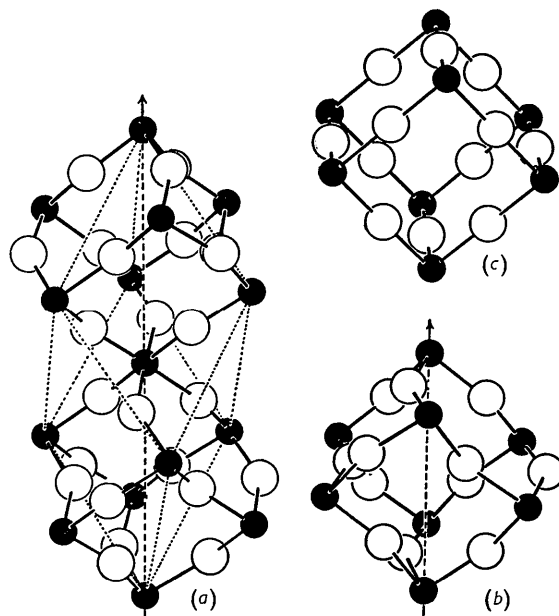
The distribution of the three types of trifluoride

Fig. 1. Comparison of the trifluoride structure types (i) and (iii). (a) The type (iii) structure, e.g. VF$_3$, FeF$_3$; (b) uni-molecular pseudo-cell of the type (iii) structure; (c) the type (i) structure, e.g. MoF$_3$, TaF$_3$. Filled circles: metal atoms; open circles: fluorine atoms. Arrows indicate the direction of [111].

structure according to the periodic classification of their metallic elements is shown in Table 4. The significance of the grouping is not clear but it is evident that each type is characteristic of a particular region of the periodic table.

In Table 5 the observed mean M–F interatomic distances for known transition-metal trifluorides are compared with the distances calculated for ionic and for covalent bonding. The ionic and covalent radii for fluorine are taken as 1·36 Å and 0·67 Å respectively. The corresponding trivalent radii for many of the metal atoms are not known with any degree of cer-tainty, but they have been assessed from data com-piled by Pauling (1940) and by Sidgwick (1950, vol. 1).

5*

Table 4. *The distribution of the three types of trifluoride structure according to the periodic classification*

(Symbols in bold type denote elements whose fluoride-type structure is known with certainty)

Group

IV	V	VI	VII	VIII		
Ti‡	V‡	Cr‡	Mn‡	Fe‡	Co‡	Ni
Zr	Nb*	Mo*	\Tc	Ru‡ /	Rh†	Pd†
Hf	Ta*	W	Re \ / Os	Ir†		Pt

* A MoF$_3$-type (i) structure.
† A PdF$_3$-type (ii) structure.
‡ A VF$_3$-type (iii) structure.

The structures of TiF$_3$ (Ehrlich & Pietzka, 1954) and CrF$_3$ (Jack, unpublished) have not been determined in detail but their types are known. Also see footnote, p. 63. MnF$_3$ has a monoclinic distortion of a VF$_3$-type (iii) structure (Hepworth & Jack, unpublished).

Table 5. *Observed and calculated mean interatomic distances in transition-metal trifluorides*

M–F (Å)

Type	Metal	Atomic number	Obs.	Calc. Ionic	Calc. Covalent	F–F(Å) Obs.
MoF$_3$	Nb	41	1·95	2·06	2·01	2·76
	Mo	42	1·95	2·06	2·03	2·76
	Ta	73	1·95	2·06	2·01	2·76
VF$_3$	V	23	1·94	2·02	1·90	2·74
	Fe	26	1·92	2·03	1·89	2·72
	Co	27	1·89	2·03	1·89	2·66
	Ru	44	1·98	2·08	2·00	2·80
PdF$_3$	Rh	45	1·98	2·05	1·99	2·79
	Pd	46	2·04	2·04	1·98	2·89
	Ir	77	2·01	2·05	1·99	2·83

In general, the observed values agree more closely with covalent distances than with ionic bond lengths. It seems probable that there is an appreciable covalent contribution to the M–F bonding. Except in the case of CoF$_3$, where least accuracy is claimed for the structure, the closest approach of fluorine atoms is never less than 2·72 Å. This is in agreement with the accepted van der Waal's radius for fluorine (*c.* 1·35 Å). The observation that the closest F–F distance is usually greater than 2·72 Å implies that the non-metal atoms are pushed apart when the interstices between them are occupied by metal atoms.

The variable composition of RuF$_3$ and IrF$_3$

The feature which distinguishes RuF$_3$ and IrF$_3$ from the remaining trifluorides is the observed variability in their unit-cell dimensions. The dimensions of five specimens of RuF$_3$ prepared under different conditions, and of two specimens of IrF$_3$ are listed in Table 6.

For RuF$_3$, the products obtained by using a large excess of reducing agent (whether iodine or sulphur) in the reduction of the pentafluoride are identical within experimental error. The decrease in the unit-cell volume observed when a deficiency of reducing agent is used is small (< 1%), but it is variable. It is possible that the larger unit cells are the result of a limited replacement of fluorine by iodine or by sulphur in the RuF$_3$ structure, but it seems unlikely that the increment would be the same in each case. Moreover, no elements other than ruthenium and fluorine were detected in any of the specimens by qualitative chemical analysis. It appears more probable that the upper limits of the cell dimensions, associated with the use of excess of different reducing agents, are those of the 'ideal' RuF$_3$. When a deficiency of reducing agent is used, it is likely that a small proportion of the ruthenium atoms in the structure are not fully reduced to the trivalent state but remain either quadrivalent or pentavalent. In order to maintain electrical neutrality, additional fluorine atoms must be incorporated into the 'ideal' structure or a corresponding number of metal-atom sites must become vacant. Since the fluorine atoms are almost close-packed, there seems little chance for the former alternative. Furthermore, a structural excess of fluorine, accommodated interstitially or by replacement of metal atoms, would cause an increase in the unit-cell volume. It seems probable, therefore, that when some ruthenium atoms exist in a valency state higher than three, electrical neutrality is maintained

Table 6. *The unit-cell dimensions of* RuF$_3$ *specimens and of* IrF$_3$ *specimens prepared by different methods*

(Dimensions of the true structural units are given in bold figures)

Method of preparation	Unimolecular rhombohedron a (Å)	Unimolecular rhombohedron α (°)	Bimolecular rhombohedron a (Å)	Bimolecular rhombohedron α (°)	Bimolecular rhombohedron V (Å³)	Hexagonal pseudo-cell a	Hexagonal pseudo-cell c	Hexagonal pseudo-cell c/a
RuF$_3$ Excess of RuF$_5$	3·659	85·24	**5·386±0·001**	**54·79±0·01**	**97·1**	4·956	13·688	2·762
Excess of RuF$_5$	3·664	85·23	**5·392±0·003**	**54·78±0·02**	**97·4**	4·961	13·705	2·763
Small excess of I$_2$	3·668	85·12	**5·403±0·003**	**54·67±0·02**	**97·7**	4·962	13·744	2·770
Large excess of I$_2$	3·672	85·13	**5·408±0·001**	**54·67±0·01**	**98·0**	4·967	13·756	2·769
Large excess of S	3·670	85·12	**5·407±0·002**	**54·66±0·02**	**97·9**	4·965	13·754	2·770
IrF$_3$ IrF$_6$+Ir → 2IrF$_3$	3·666	84·72	**5·418±0·002**	**54·13±0·03**	**97·3**	4·940	13·819	2·797
2IrF$_4$ → 2IrF$_3$+F$_2$	3·667	84·78	**5·417±0·003**	**54·31±0·06**	**97·5**	4·945	13·810	2·793

by a structural deficiency of ruthenium. The unit-cell volume would then be decreased in accordance with the observations.

For these reasons it seems justifiable to assume that the 'ideal' RuF_3 structure has the rhombohedral dimensions $a = 5\cdot408\pm0\cdot001$ Å, $\alpha = 54\cdot67\pm0\cdot01°$.

When the structure is referred to hexagonal axes (see Table 6), it is seen that the dimensional decrements due to cationic vacancies are such that the axial ratio c/a decreases with decreasing unit-cell volume. In the 'ideal' structure, each RuF_6 octahedron is not perfectly regular but is expanded by the presence of the cation by about $0\cdot3\%$ along its trigonal (c hexagonal) axis. The removal of a ruthenium atom from an octahedral interstice, and also the substitution of a trivalent metal atom by a smaller one of higher valency, might therefore be expected to decrease the c dimension to a larger extent than the a dimension. This evidence is not offered as a positive confirmation of the proposed explanation for the variability in the cell-volumes of different RuF_3 preparations, but at least it is not in contradiction to the other experimental observations. The occurrence of divalent cations in the RuF_3 structure can be discounted since scarcely any simple compounds of divalent ruthenium are known (Sidgwick, 1950, vol. 2).

The unit-cell dimensional differences for the two preparations of IrF_3 (see Table 6) are very small ($< 0\cdot2\%$), and therefore their occurrence is less readily explicable than in the case of RuF_3. Again it is plausible to assume the existence in the structure of a small number of cations with valency states differing from three. For iridium, however, the difluoride is said to be one of the products obtained not only by decomposing IrF_4 but also by the reaction of IrF_6 with iridium metal (Sidgwick, 1950, vol. 2). Since these were the two methods of preparation used in the present work and which gave slightly different products, it is possible that cations with valency states both lower and higher than three may be accommodated in the IrF_3 structure. Only one-third of the available interstices are occupied at the stoichiometric composition, and (unlike RuF_3) the empty octahedral holes are just as large as the filled ones. The larger axial ratio of the fluoride prepared from IrF_6 and metallic iridium could be accounted for by a structural excess of divalent cations. Both specimens, however, have unit-cell volumes ($97\cdot3\pm0\cdot1$ Å³ and $97\cdot5\pm0\cdot2$ Å³) which are identical within experimental error.

Variations in the compositions of other transition-element trifluorides have not been observed in the present investigation but their dimensions are appreciably different from those reported for FeF_3, CoF_3, RhF_3 and PdF_3 by Ebert in his early work (1931). It is also of interest that a specimen of FeF_3 with cell-dimensions $a = 5\cdot349$ Å and $\alpha = 58\cdot08°$ has been prepared recently at Uppsala (Hägg, 1955). The differences between these values and our own ($a = 5\cdot362\pm0\cdot001$ Å, $\alpha = 57\cdot98\pm0\cdot01°$) are well outside the limits of experimental error. It may be not without significance that the fluorinating agent employed in the preparative work described in the present paper is elementary fluorine used under strictly anhydrous conditions. When hydrogen fluoride is used, and when air and moisture are not rigorously excluded from the apparatus, it seems possible that hydroxyl groups or oxygen atoms might replace fluorine in the fluoride structures.

References

AYNSLEY, E. E., PEACOCK, R. D. & ROBINSON, P. L. (1952). *Chem. Ind.* p. 1002.

EBERT, F. (1931). *Z. anorg. Chem.* **196**, 398.

EHRLICH, P. & PIETZKA, G. (1955). *Z. anorg. Chem.* **275**, 121.

EHRLICH, P., PLÖGER, F. & PIETZKA, G. (1954). *Z. anorg. Chem.* **282**, 19.

GUTMANN, V. & JACK, K. H. (1951). *Acta Cryst.* **4**, 244.

HÄGG, G. (1955). Private communication.

International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.

JACK, K. H. & GUTMANN, V. (1951). *Acta Cryst.* **4**, 246.

KETELAAR, J. A. A. (1933). *Z. Kristallogr.* **85**, 119.

NOWACKI, W. (1939). *Z. Kristallogr.* **101**, 273.

PAULING, L. (1940). *The Nature of the Chemical Bond*, 2nd ed. London: Oxford University Press.

SIDGWICK, N. V. (1950). *The Chemical Elements and their Compounds*. Oxford: Clarendon Press.

SIEGEL, S. (1956). *Acta Cryst.* **9**, 684.

TAYLOR, A. (1951). *J. Sci. Instrum.* **28**, 200.

WOOSTER, N. (1933). *Z. Kristallogr.* **84**, 320.

WYCKOFF, R. W. G. (1948). *Crystal Structures*, vol. 1. New York: Interscience Publishers.