configuration pseudo-symétrique et les longueurs anormalement courtes des liaisons hydrogène suggèrent une distribution des charges sur les atomes de NO_3 intermédiaire entre celle de l'ion NO_3^-, et celle de la molécule HNO_3 à l'état gazeux et dans les cristaux d'acide anhydre.

On remarque sur le tableau suivant que les molécules HNO_3 de l'acide anhydre sont plus éloignées de la symétrie ternaire que celles de l'acide à une molécule d'eau, bien que les différences soient à la limite de l'erreur de mesure.

	N–OH	N–O
HNO_3	1,30 A.; 134°	1,24 A.; 113°
$HNO_3.H_2O$	1,29 A.; 127°	1,22 A.; 116,5°

Bibliographie

Bouttier, L. (1949). *C.R. Acad. Sci., Paris*, **228**, 1419.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Cruickshank, D. W. J. (1950). *Acta Cryst.* **3**, 10.

Grison, E., Eriks, K. & Vries, J. L. de (1950). *Acta Cryst.* **3**, 290.

Luzzati, V. (1951). *Acta Cryst.* **4**, 120.

Acta Cryst. (1951). **4**, 244

The Crystal Structures of Molybdenum Trifluoride, MoF_3, and Tantalum Trifluoride, TaF_3

By V. Gutmann* and K. H. Jack

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

(*Received* 14 *September* 1950)

Molybdenum trifluoride and tantalum trifluoride are isostructural with rhenium trioxide, ReO_3. The cubic unit cell, with space group *Pm*3*m*, contains one metal atom at 0, 0, 0 and three fluorine atoms at ½, 0, 0; 0, ½, 0; and 0, 0, ½. The structure consists of regular octahedra of fluorine atoms, each with a metal atom at its centre, joined by sharing corners only. The structure is alternatively described as a cubic close-packing of fluorine atoms in which one-quarter of the octahedral interstices are occupied by metal atoms and in which one-quarter of the fluorine atom sites remain vacant. For MoF_3, $a = 3{\cdot}8985 \pm 0{\cdot}0005$, Mo–F = 1·949 and F–F = 2·757 A. For TaF_3, $a = 3{\cdot}9012 \pm 0{\cdot}0002$, Ta–F = 1·951 and F–F = 2·759 A.

Introduction

The anhydrous trifluorides of molybdenum and tantalum, MoF_3 and TaF_3, have recently been prepared by Emeléus & Gutmann (1949, 1950). Of the trifluorides of the transition elements, the only structures which have previously been investigated are those of scandium, iron, cobalt, palladium and rhodium trifluorides. Scandium trifluoride has a rhombohedrally distorted rhenium trioxide (ReO_3) structure (Nowacki, 1939). Some workers (Wooster, 1933; Nowacki, 1939) consider FeF_3, CoF_3, PdF_3 and RhF_3 also to have this distorted ReO_3 structure with an approximately cubic close-packing of fluorine atoms. Others (Ebert, 1931; Ketelaar, 1931, 1933) consider these fluorides to be similar to aluminium trifluoride, AlF_3, in which the fluorine atoms are in considerably distorted hexagonal close-packing. Wyckoff (1948, section 1, chap. 5, text p. 13) states that the results of the relevant published analyses are confusing and he emphasizes the need for further study of these crystals.

In the present and subsequent papers quantitative X-ray investigations of several fluorides of transitional elements are described. The results offer new structural data and resolve some previous difficulties.

Experimental

Powder photographs of molybdenum and tantalum trifluorides, prepared by Emeléus & Gutmann (1949, 1950), were taken at 18 ± 2° C. in a 9 cm. cylindrical camera using Fe $K\alpha$ monchromatic radiation (α_1, 1·93597; α_2, 1·93991 A.) from synthetic lithium fluoride (200) planes. The films, which showed a low background intensity, were microphotometered with a Dobson-type instrument (1923) and values of integrated intensities in arbitrary units were obtained by measuring areas under the photometer curves with a planimeter.

For any line in a powder photograph the intensity is given by

$$I = \text{constant}\,.\,F^2_{hkl}\,.\,\frac{1+\cos 2\alpha\,.\,\cos^2 2\theta}{\sin^2\theta\,.\,\cos\theta}\,.\,p\,.\,A \times \exp\left[-B(\sin\theta/\lambda)^2\right],$$

where α is the angle of reflexion in the monochromator, and other symbols have their usual meanings. In calculating intensities, the absorption-edge effect was found from Hönl's formula (see James, 1948, vol. 2, pp. 160, 608) and absorption and arbitrary temperature factors were obtained in the normal way (Bradley, 1935; Bradley & Lu, 1937). Unit-cell dimensions were calculated by the extrapolation method of Nelson & Riley (1945).

---

* Now at Institut für allgemeine Chemie, Technische Hochschule, Vienna VI, Austria.

Results

All observed X-ray reflexions from molybdenum trifluoride and from tantalum trifluoride were indexed on a simple cubic unit cell. With Fe $K\alpha$ radiation the occurrence of the (400) reflexions at Bragg angles greater than 83° enabled the cell dimensions to be calculated with a high degree of accuracy.

For MoF_3, $a = 3{\cdot}8985 \pm 0{\cdot}0005$ A.,
for TaF_3, $a = 3{\cdot}9012 \pm 0{\cdot}0002$ A.

Values of $\sin^2\theta$ calculated from these dimensions and corrected for systematic errors (see Heavens & Cheesman, 1950; also Taylor & Floyd, 1950) are compared with observed $\sin^2\theta$ values in Table 1.

Trial-and-error methods showed that molybdenum and tantalum trifluorides are isostructural, the unit cell containing in each case one metal atom at 0, 0, 0 and three fluorine atoms at $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; and $0, 0, \frac{1}{2}$. As shown in Table 1, relative intensities calculated for this structure are in excellent agreement with the observed intensities.

Table 1. *Calculated and observed X-ray data for molybdenum and tantalum trifluorides*

(Fe $K\alpha$ radiation.)

	MoF_3				TaF_3			
	$\sin^2\theta$		Relative intensities		$\sin^2\theta$		Relative intensities	
hkl	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
100	0·0628	0·0625	216	227	0·0626	0·0619	181	181
110	0·1249	0·1240	88	94	0·1245	0·1241	129	127
111	0·1868	0·1858	13	14	0·1863	0·1854	37	38
200	0·2487	0·2487	76	75	0·2480	0·2478	73	73
210	0·3105	0·3101	133	125	0·3098	0·3098	169	158
211	0·3722	0·3725	53	52	0·3714	0·3714	100	92
220	0·4955	0·4957	60	47	0·4945	0·4945	76	78
300 221	0·5572	0·5575	87	86	0·5561	0·5559	136	145
310	0·6188	0·6190	33	34	0·6177	0·6181	78	80
311	0·6803	0·6803	13	17	0·6792	0·6792	55	63
222	0·7419	0·7419	30	25	0·7407	0·7406	48	48
320	0·8034	0·8044	60	53	0·8021	0·8023	119	114
321	0·8649	0·8651	74	77	0·8636	0·8638	207	208
400	0·9878	0·9878	—	—	0·9865	0·9865	—	—

Discussion of the MoF_3 and TaF_3 structures

The proposed structures for MoF_3 and TaF_3 are identical with that of ReO_3, space group *Pm*3*m*. Each metal atom is surrounded by an octahedron of six equidistant fluorine atoms. Fig. 1 shows that these co-ordination octahedra are joined by sharing corners only. Each fluorine has two metal atom nearest neighbours and eight equidistant fluorine atom neighbours. A feature of the structure is the large 'hole' at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Occupation of this site by an additional fluorine atom would result in a perfect cubic close-packing of the non-metal atoms. In the related perovskite structure, ABX_3, this same interstice is occupied by the larger metal atom A. The MoF_3 or TaF_3 structure may therefore be described as a cubic close-packing of fluorine atoms in which one-quarter of the octahedral interstices are occupied by metal atoms forming a simple cubic superlattice, and in which one-quarter of the fluorine atom sites—those not adjacent to metal atoms—remain vacant.

Nearest interatomic distances are:

for MoF_3, Mo–Mo = 3·899 A.; Mo–F = 1·949 A.; F–F = 2·757 A.;

for TaF_3, Ta–Ta = 3·901 A.; Ta–F = 1·951 A.; F–F = 2·759 A.

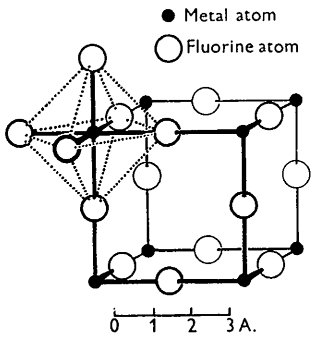

Fig. 1. The structure of molybdenum and tantalum trifluorides.

Although there are no reliable values for the ionic radii of trivalent molybdenum and tantalum they must be of the order of 0·7 A. Taking the ionic radius of fluorine as 1·36 A., the sum of the metal and non-metal ionic radii is about 2·06 A. If unionized radii are used ($r_{Mo} = 1{\cdot}36$; $r_{Ta} = 1{\cdot}42$–$1{\cdot}44$; $r_F = 0{\cdot}67$ A.), the sum is not greatly different, namely, about 2·1 A. In calculating the intensities of X-ray reflexions, agreement with the observed intensities is slightly better using scattering factors for unionized atoms than when ionic scattering factors are used, but the difference cannot be regarded as significant. It is likely that the bonding is partly ionic and partly covalent in character, in which case the metal–non-metal interatomic distance would probably be smaller than for completely covalent or completely ionic bonding. The observed value of 1·95 A. therefore supports this view. The nearest approach of fluorine atoms, 2·757 and 2·759 A. in MoF_3 and TaF_3 respectively, is not inconsistent with the accepted value of 1·36 A. for the fluorine ionic radius, but since the metal atoms will probably force the non-metal atoms apart, the effective size of the fluorine atoms in these structures cannot be deduced from their distances of closest approach.

References

Bradley, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.

Bradley, A. J. & Lu, S. S. (1937). *Z. Krystallogr.* **96**, 20.

Dobson, G. M. B. (1923). *Proc. Roy. Soc.* A, **104**, 248.

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

Emeléus, H. J. & Gutmann, V. (1949). *J. Chem. Soc.* p. 2979.

Emeléus, H. J. & Gutmann, V. (1950). *J. Chem. Soc.* p. 2115.

Heavens, O. S. & Cheesman, G. H. (1950). *Acta Cryst.* **3**, 197.

James, R. W. (1948). *The Crystalline State.* London: Bell and Sons.

Ketelaar, J. A. A. (1931). *Nature, Lond.*, **128**, 303.

Ketelaar, J. A. A. (1933). *Z. Krystallogr.* **85**, 119.

Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.

Nowacki, W. (1939). *Z. Krystallogr.* **101**, 273.

Taylor, A. & Floyd, R. W. (1950). *Acta Cryst.* **3**, 245.

Wooster, N. (1933). *Z. Krystallogr.* **84**, 320.

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

Acta Cryst. (1951). **4**, 246

The Crystal Structure of Vanadium Trifluoride, VF_3

By K. H. Jack and V. Gutmann*

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

(*Received* 14 *September* 1950)

The unit cell of vanadium trifluoride, VF_3, is rhombohedral with dimensions $a = 5{\cdot}373 \pm 0{\cdot}002$ A., $\alpha = 57{\cdot}52 \pm 0{\cdot}03°$. The structure places atoms in the following special positions of space group $R\bar{3}c$:

$$2\ \text{V atoms at } 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}, \text{ and}$$

$$6\ \text{F atoms at } \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4});\ \pm(\tfrac{1}{2}-x, \tfrac{1}{4}, x);\ \pm(\tfrac{1}{4}, x, \tfrac{1}{2}-x),$$

with $x = -0{\cdot}145 \pm 0{\cdot}015$ Direct experimental evidence shows that the structural unit is not the unimolecular rhombohedron proposed by some workers for the isomorphous FeF_3, CoF_3, RhF_3 and PdF_3. Preliminary observations indicate that CoF_3 has a bimolecular unit cell and is isostructural with VF_3. The VF_3 structure is not identical either to that of AlF_3 or to that of the ScF_3, MoF_3 and TaF_3 group, but has relationships with each of these structure types. Almost regular octahedra of fluorine atoms, each with a vanadium atom at its centre, are joined by sharing corners only. The fluorine atoms are not close-packed, and although their arrangement approximates to a hexagonal close-packing rather than to a cubic close-packing, it can be derived from the latter by relatively small atomic movements and by omission of atoms from certain sites. Principal interatomic distances are

$$\text{V–V} = 3{\cdot}73;\quad \text{F–F} = 2{\cdot}74 \text{ and } 2{\cdot}75;\quad \text{V–F} = 1{\cdot}95\ \text{A.}$$

Introduction

Vanadium trifluoride, VF_3, was first prepared by Ruff & Lickfett (1911) by the action of anhydrous hydrogen fluoride on vanadium trichloride at red heat. The present X-ray work is the first on this fluoride and was carried out on pure specimens obtained in a recent chemical investigation (Emeléus & Gutmann, 1949) with which one of us was associated.

Preliminary observations suggested that VF_3 is isostructural with the trifluorides of iron, cobalt, rhodium and palladium, but since the structures of these are not yet fully established (see Wyckoff, 1948, section 1, chap. 5, text p. 13) a complete investigation of the vanadium compound seemed desirable. The structures proposed for FeF_3, CoF_3, RhF_3 and PdF_3 by Ebert (1931) (*Strukturbericht*, 1937 *a*, *b*) were based solely upon spatial and symmetry considerations and are found to be incompatible with the observed intensities of X-ray reflexions. All observed reflexions were indexed on a rhombohedral cell containing only one molecule, but the proposed structure requires a larger bimolecular unit cell, space group $R\bar{3}c$, the dimensions of which are given in Table 1. The given parameters, i.e.

$$2\ \text{metal atoms at } 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}, \text{ and}$$

$$6\ \text{F atoms at } \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4});\ \pm(\tfrac{1}{2}-x, \tfrac{1}{4}, x);\ \pm(\tfrac{1}{4}, x, \tfrac{1}{2}-x),$$

with $x = -\frac{1}{12}$, indicate a slightly distorted hexagonal close-packing of the fluorine atoms with the metal atoms occupying certain octahedral interstices and forming a rhombohedrally distorted simple-cubic superlattice. The structure of aluminium trifluoride has been

---

* Now at Institut für allgemeine Chemie, Technische Hochschule, Vienna VI, Austria.