

The Structures of Yttrium and Bismuth Trifluorides by Neutron Diffraction

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The crystal structures of YF₃ and BiF₃ have been re-examined by powder neutron diffraction. The positional and thermal parameters were refined by a least-squares method based on profile intensities. The cell constants from Guinier X-ray diagrams are

YF₃: $a = 6.3537(7)$, $b = 6.8545(7)$, $c = 4.3953(5)$ Å.
BiF₃: $a = 6.5605(4)$, $b = 7.0155(4)$, $c = 4.8416(2)$ Å.
Space group *Pnma*

In YF₃, yttrium has eight nearest neighbours at distances between 2.281 Å and 2.310 Å and a ninth at 2.538 Å. In BiF₃, the eight corresponding distances vary between 2.217 Å and 2.502 Å but the ninth fluorine is at 3.100 Å. The possibility that the lone pair of electrons on bismuth is stereochemically active is considered.

1. INTRODUCTION

The trifluorides of the rare-earth elements from samarium to lutetium adopt the orthorhombic YF₃-type structure at room temperature.¹ A single crystal X-ray study of YF₃ by Zalkin and Templeton² suggests that yttrium has eight nearest neighbour fluoride ions at distances between 2.25 and 2.32 Å with a further neighbour at 2.60 Å. However, the exact details of this structure are still uncertain since in the mentioned work the fluoride ions were located on the basis of geometrical considerations alone. We have therefore undertaken a detailed neutron diffraction study of YF₃.

Bismuth trifluoride is reported to be isostructural with YF₃ but the positions of the fluoride ions have not been established.³ This compound is particularly interesting since it is well known that in the oxides and oxyfluorides

of tin(II), lead(II), antimony(III), and bismuth(III), the lone pair of electrons on the metal ion is stereochemically active.⁴ In order to examine the possibility of such behaviour in BiF₃, we have also carried out a precise structure determination of this compound.

2. EXPERIMENTAL

2.1 Sample preparation. The YF₃ was obtained as a specpure material from Koch-Light Ltd. BiF₃ was prepared from Bi₂O₃ and 40 % HF solution in the manner described by Aurivillius.³

2.2 X-Ray data. The compounds crystallize in space group *Pnma*.

The unit cell dimensions of the compounds were determined from Guinier patterns taken with CuK α_1 radiation and with KCl as internal standard. The values and standard deviations obtained from least-squares refinements were

YF₃: $a = 6.3537(7)$, $b = 6.8545(7)$, $c = 4.3953(5)$ Å
BiF₃: $a = 6.5605(4)$, $b = 7.0155(4)$, $c = 4.8416(2)$ Å

2.3 Neutron diffraction experiments. Powder neutron diffraction experiments were carried out on YF₃ and BiF₃ at room temperature using the PANDA diffractometer at A.E.R.E. Harwell. Data were collected over a range of 2θ from 20 to 100 degrees in steps of 1/50 degree. A monitor was used to register the intensity of the direct beam and integrated counts were printed out every 1/10 degree. The recording rate was approximately 1.5 degrees per hour. A neutron wavelength of 1.504 Å was obtained by reflection from the (331) planes of a germanium monochromator at a take-off angle of 72 degrees. The measurements comprised 105 reflections for YF₃ and 131 reflections for BiF₃. The maximum counts observed were 5000 for YF₃ and 7000 for BiF₃, the background for each compound being

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almost constant at 500 and 600 counts, respectively. Absorption effects were negligible and no corrections were necessary.

3. REFINEMENTS

The structural parameters were refined by a full-matrix least-squares analysis of the powder diffraction profile.⁵⁻⁶ In this method, each Bragg reflection is assumed to be gaussian in shape and the profile is calculated from the sum of gaussian peaks corresponding to the set of reflections. Thus, each intensity observation is the sum of the contributions from the reflections which overlap at that point, and the weighted difference between the observed and calculated profiles is minimized by least-squares. The unit cell dimensions, diffractometer zero-point error and three instrumental half-width parameters⁶ are refined simultaneously with the atomic positional and thermal parameters.

The starting values for the analysis were taken from the work by Zalkin and Templeton² with the space group *Pnma*. Independent isotropic Debye-Waller factors for all atoms were included as variables. Scattering lengths of 0.79, 0.86, and 0.574 ($\times 10^{-14}$ m) were used for yttrium, bismuth, and fluorine, respectively.⁷ Final structural parameters for YF₃ and BiF₃ are given in Tables 1 and 2. The reliability factors based upon the profile ($R_{pr} = 100 \sum (y_i^o - y_i^c) / \sum y_i^o$) are 8.39 % and 8.65 % for YF₃ and BiF₃,

respectively. Estimates of the more conventional reliability factors based upon the intensities of the Bragg reflections ($100 \sum |F_o^2 - F_c^2| / \sum F_o^2$) are 3.99 % for YF₃ (105 reflections) and 4.68 % for BiF₃ (131 reflections). The final observed and calculated diffraction profiles for YF₃ and BiF₃ are shown in Figs. 1 and 2.

4. SPACE GROUP AMBIGUITY

The measurements showed that (*0kl*)-reflections were observed only for $k+l=2n$ and (*hk0*)-reflections only for $h=2n$. Thus the centric space group *Pnma* and the non-centric *Pn2₁a* are both possible. Nyburg *et al.*⁸ conclude that molecular BiCl₃ crystallizes in the latter space group and recommend that the structures of other group V trihalides be re-examined.

Refinements based on space group *Pn2₁a* were carried out for both YF₃ and BiF₃. For starting values the parameters were removed from their centric positions in order to reduce correlation effects. The refinements converged towards a model very close to the centric one, the shifts in atomic positions being less than 0.1 Å and in the same directions for corresponding atoms in the two compounds. The apparent deviations from centric symmetry were similar to those reported for BiCl₃. With 5 more parameters to refine the *R*(profile) factors dropped

Table 1. Atomic coordinates and thermal parameters (B) for YF₃. Standard deviations in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Yttrium	0.3673(4)	0.25	0.0591(5)	0.37(5)
Fluorine(1)	0.5227(5)	0.25	0.5910(8)	0.89(7)
Fluorine(2)	0.1652(4)	0.0643(3)	0.3755(5)	0.57(5)

Table 2. Atomic coordinates and thermal parameters (B) for BiF₃. Standard deviations in parentheses.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Bismuth	0.3554(4)	0.25	0.0359(4)	0.46(4)
Fluorine(1)	0.5392(6)	0.25	0.6257(8)	1.49(8)
Fluorine(2)	0.1662(4)	0.0581(4)	0.3532(6)	1.20(5)

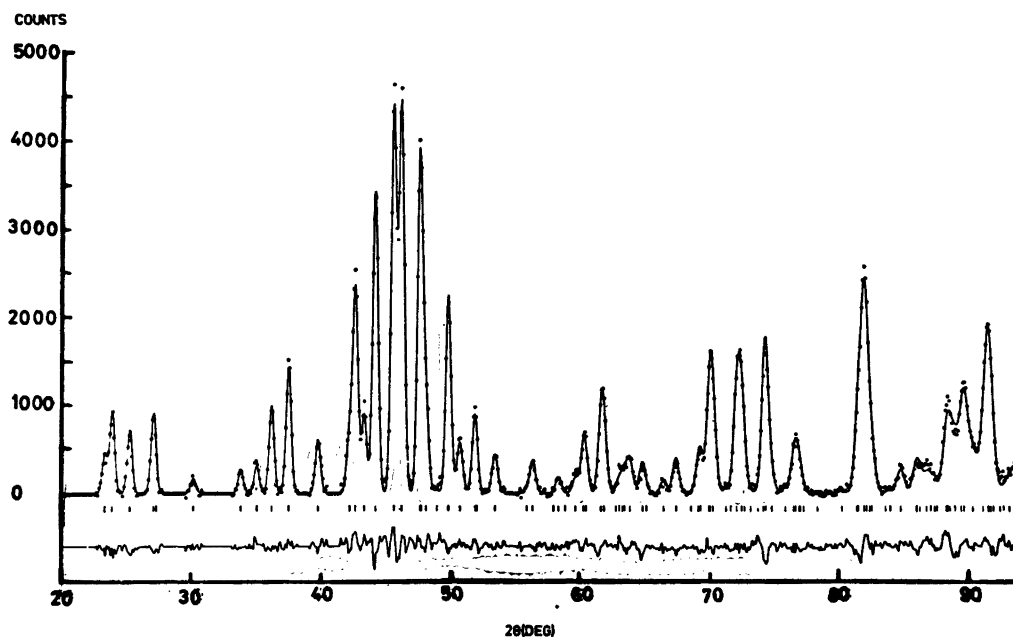


Fig. 1. The observed and calculated diffraction profiles for YF_3 (observed profile-dots; calculated profile-smooth curves). The difference profile and reflection positions are also shown.

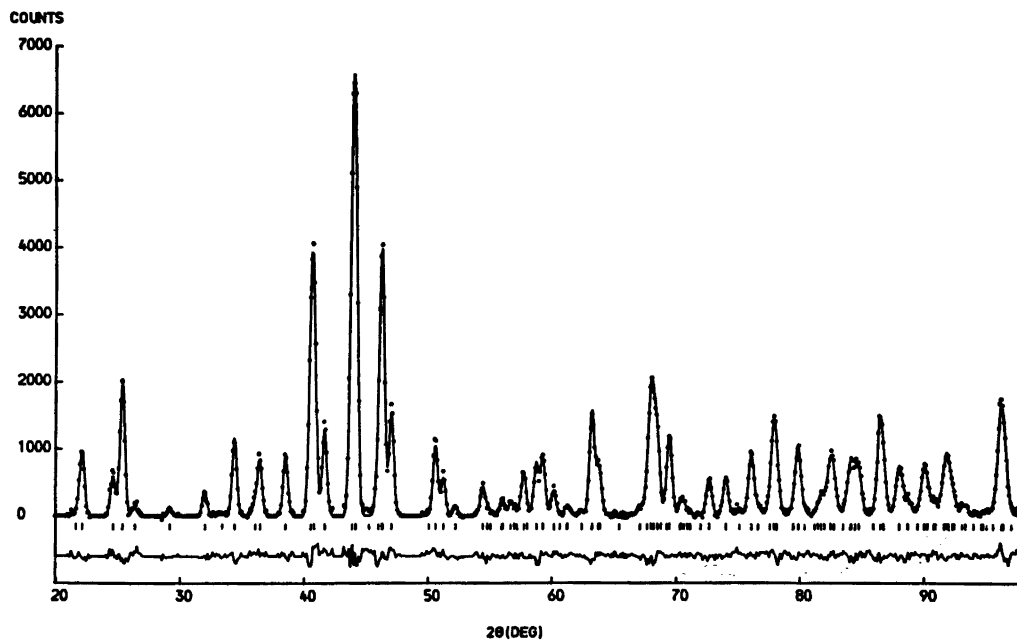


Fig. 2. The observed and calculated diffraction profiles for BiF_3 (observed profile-dots; calculated profile-smooth curve). The difference profile and reflection positions are also shown.

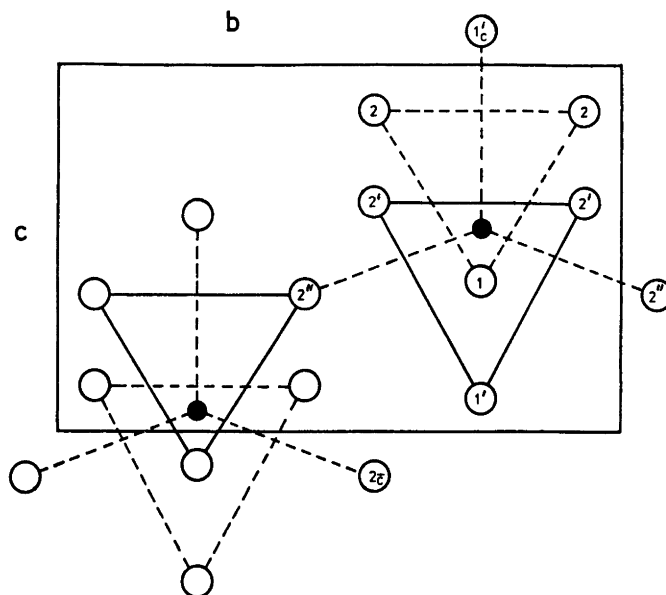


Fig. 3. Projection of the YF_3 structure down the a -axis.

from 8.39 and 8.65 to 8.27 and 8.53 % for YF_3 and BiF_3 , respectively. Due to strong positional correlations between the previously mirror-related fluoride ions, the standard deviations increased by as much as a factor of 8 and a larger spread of calculated metal-fluorine distances was also found. Even though both models are chemically reasonable, considering the very small shifts and the large standard deviations, we found insufficient evidence for preferring the non-centric space group. All our later discussions of the structures are thus based on space group $Pnma$.

5. DISCUSSION OF THE STRUCTURES

5.1 Yttrium trifluoride. The arrangement of the atoms is demonstrated by the projection along the a -axis shown in Fig. 3. The yttrium ion has nine nearest-neighbour fluoride ions comprising a slightly deformed trigonal prism with atoms opposite each of the lateral faces as reported by Zalkin and Templeton.³ In Table 3 the computed interatomic distances show that eight of the nearest neighbours lie at distances between 2.281 Å [$\text{Y}-\text{F}(2)$] and 2.310 Å [$\text{Y}-\text{F}(2'')$]. The ninth distance [$\text{Y}-\text{F}(1_c')$] of 2.538 Å as compared to 2.60 Å in the previous work

Table 3. Interatomic distances (in Å) with standard deviations.

Distance ^a	YF_3	BiF_3
Metal - F(1)	2.287(4)	2.217(5)
Metal - F(2)	2.281(3)	2.390(3)
Metal - F(1')	2.282(4)	2.323(5)
Metal - F(1 _c)	2.538(4)	3.100(5)
Metal - F(2')	2.299(3)	2.502(3)
Metal - F(2'')	2.310(2)	2.340(3)
Metal - F(2 _c)	3.507(3)	3.779(3)
F(1) - F(2)	2.578(4)	2.808(4)
F(1) - F(2'')	2.932(3)	2.901(4)
F(2) - F(2)	2.546(3)	2.693(3)
F(2) - F(1 _c)	2.771(4)	3.089(5)
F(2) - F(2')	3.363(4)	3.429(4)
F(2) - F(2'')	2.601(3)	2.781(4)
F(1') - F(2')	2.818(4)	2.979(5)
F(1') - F(2'')	2.762(3)	2.775(4)
F(2') - F(2'')	2.526(3)	2.728(4)

^a A subscript refers to an axial translation of an atom.

can hardly be said to be exceptionally long, so that the yttrium ion in YF_3 can be considered to have genuine 9 coordination. From the same table is seen that the next shortest fluorine distance is 3.507 Å [$\text{Y}-\text{F}(2_c)$]. The triangular

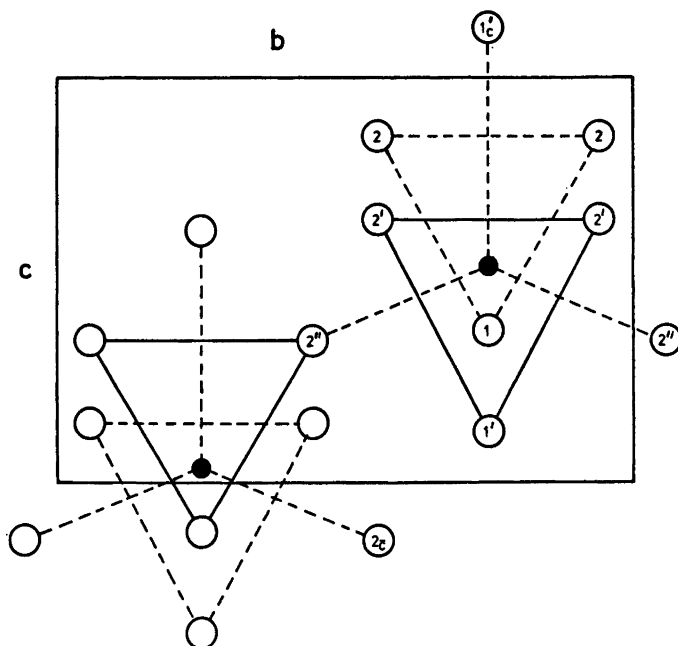


Fig. 4. Projection of the BiF_3 structure down the a -axis.

bases of the trigonal prism are almost parallel (2.60°), but there are small deviations from threefold symmetry. The distance between nearest neighbour fluoride ions varies between 2.526 \AA [$\text{F}(2')\text{--F}(2'')$] and 2.932 \AA [$\text{F}(1)\text{--F}(2'')$].

5.2 Bismuth trifluoride. A projection of the BiF_3 structure on to the bc plane is shown in Fig. 4 and the interatomic distances are given in Table 3. In contrast to the metal coordination in YF_3 , bismuth has eight nearest neighbour fluoride ions at distances between 2.217 \AA [$\text{Bi}\text{--F}(1)$] and 2.502 \AA [$\text{Bi}\text{--F}(2')$] with the ninth ion now at 3.100 \AA . Bismuth can therefore be described as 8-coordinated. It is attractive to postulate that the distortion of the coordination sphere compared with that in YF_3 stems from the stereochemical activity of the lone pair of electrons on bismuth. This type of behaviour is normally associated with an anomalously high unit cell volume⁴ and a comparison of the cell volumes of BiF_3 (222.8 \AA^3) and EuF_3 (204.3 \AA^3) reveals such an anomaly in the bismuth compound (Eu^{3+} has approximately the same ionic radius as bismuth⁹). It would therefore appear

that the lone pair protrudes along the $\text{Bi}\text{--F}(1')$ direction giving rise to the exceptionally long $\text{Bi}\text{--F}(1')$ distance and the elongation of the c -axis. It should also be noted that the $\text{Bi}\text{--F}(2)$ and $\text{Bi}\text{--F}(2')$ distances are rather longer than expected. The shortest $\text{F}\text{--F}$ distances vary between 2.693 \AA [$\text{F}(2)\text{--F}(2)$] and 3.089 \AA [$\text{F}(2)\text{--F}(1')$]. The larger spacings between nearest-neighbour fluoride ions in BiF_3 are reflected in the larger Debye-Waller factors for fluorine (Table 2).

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REFERENCES

1. Thoma, R. E. and Brunton, G. D. *Inorg. Chem.* 5 (1966) 1937.
2. Zalkin, A. and Templeton, D. H. *J. Amer. Chem. Soc.* 75 (1953) 2453.
3. Aurivillius, B. *Acta Chem. Scand.* 9 (1955) 1206.
4. Andersson, S. and Åström, A. *NBS Special Publication 364*, Solid State Chemistry 1972.
5. Rietveld, H. M. *Acta Crystallogr.* 22 (1967) 151.
6. Rietveld, H. M. *J. Appl. Cryst.* 2 (1969) 65.
7. Neutron Diffraction Commission, *Acta Crystallogr. A* 25 (1969) 391.
8. Nyburg, S. C., Ozin, G. A. and Szymański, J. T. *Acta Crystallogr. B* 27 (1971) 2298.
9. Shannon, R. D. and Prewitt, C. T. *Acta Crystallogr. B* 25 (1969) 925.

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