The Crystal Structure of Iodine Oxide Trifluoride

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ON the basis of the similarity of the decomposition of iodine oxide trifluoride and of potassium hexafluoroiodate(v), it has been suggested[1] that IOF_3 exists as the ionic $[IO_2]^+ [IF_6]^-$. We report here *X*-ray crystallographic data which show IOF_3 to have a molecular configuration similar to that of the $IO_2F_2^-$ anion.[2]

IOF_3 was prepared by the method of Aynsley,[1] and the white crystals obtained were sealed in glass capillaries in a dry nitrogen atmosphere to prevent reaction of the hygroscopic compound with atmospheric moisture. Five levels of Weissenberg film data resulting in 275 independent observed reflections were obtained using Mo-K_α radiation. IOF_3 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 5{\cdot}638$, $b = 5{\cdot}689$, $c = 10{\cdot}463$ Å, and $Z = 4$. The iodine positions were obtained from a three-dimensional Patterson synthesis and the light atoms were placed by successive electron-density and difference-Fourier syntheses. The structure was refined using the Busing–Levy–Martin least-squares programme[3] which we modified to include corrections for anomalous dispersion effects. The final discrepancy factors[3] are $R_1 = 0{\cdot}074$ and $R_2 = 0{\cdot}082$.

The configuration of the IOF_3 molecule can be described as a trigonal bipyramid distorted due to the influence of the nonbonding pair of electrons (see Figure and Table). Similarity in the scattering abilities of fluorine and oxygen atoms gives rise to ambiguity in the assignment of these atoms from the electron-density maxima. The position assigned as the oxygen atom position was verified by carrying out two separate refinements with the oxygen atom alternately in each of the two possible equatorial sites. The oxygen atom was restricted to the equatorial plane since in other trigonal bipyramid structures the axial sites are found to be occupied by the more electronegative atoms.[4]

The I–O bond distance is 1·82 Å which is much shorter than the value of 1·93 Å found for this bond in the KIO_2F_2 study[2] but is in good agreement with the distances reported for this bond in a number of recent studies.[5] The I–F bond distances are also considerably shorter than the value of 2·03 Å found for this bond in KIO_2F_2. These values, however, are in good agreement with I–F distances reported for IF_7.[6] The axial I–F bonds are longer by four to seven standard deviations than the equatorial I–F bond, as expected qualitatively for a trigonal bipyramid structure. Many intermolecular I · · · F contracts are considerably less than the sum (3·5 Å) of the van der Waals radii,[7] indicating the likelihood of strong intermolecular attractions, the atoms F(1) and F(3) being particularly implicated.

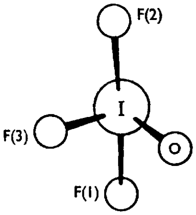

FIGURE. *The molecular configuration of* IOF_3.

TABLE. *Intramolecular distances and angles.*

(*Standard deviations of distances* ~0·02 Å *and standard deviations of angles* ~1°)

I–F(1)	1·90 Å	F(1)–I–F(2)	168°
I–F(2)	1·83	F1–I–F(3)	90°
I–F(3)	1·74	F(1)–I–O	82°
I–O	1·82	F(2)–I–F(3)	95°
		F(2)–I–O	86°
		F(3)–I–O	98°

This research was supported by the National Science Foundation.

(*Received, August* 16*th*, 1967; *Com.* 885.)

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