# Crystal Structure of $CF_3I(Cl)F$

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In addition to $CF_3IF_2$ and $CF_3ICl_2$, $CF_3I(Cl)F$ is the only known example of the (trifluoromethyl)iodine dihalides. $CF_3I(Cl)F$ is even at low temperatures not stable in solution and decomposes by symmetrization. It crystallizes in the orthorhombic space group *Cmca* with $a = 6.898(1)$ Å, $b = 7.310(1)$ Å, $c = 20.127(1)$ Å and eight formula units per unit cell. The final $R$ indices $[I > 2\sigma(I)]$ are R1 = 0.0372 and wR2 = 0.0981.

## Introduction

Recently we reported the crystal structures of $CF_3IF_2$ and $CF_3ICl_2$.[1,2] In this work, we present the crystal structure of $CF_3I(Cl)F$, the only known example of a ternary interhalogen compound containing a $CF_3$ group.

$CF_3I(Cl)F$ was first prepared in 1995 by the reaction of trifluoromethyl iodide ($CF_3I$) with trifluoromethyl hypochlorite ($CF_3OCl$) at −78 °C.[3] It was characterized by vibrational spectroscopy and NMR spectroscopy. The NMR spectra show that, even at low temperatures, $CF_3I(Cl)F$ is not stable in solution, decomposing to the symmetrical dihalides, $CF_3IF_2$ and $CF_3ICl_2$. For this reason, attempts to recrystallize $CF_3I(Cl)F$ are very difficult and the preparation cited above yields $CF_3I(Cl)F$ in a microcrystalline form, unsuitable for an X-ray diffraction study.

$CF_3I(Cl)F$ can be considered as a derivative of $IF_2Cl$ or $IFCl_2$, whose existence has not been confirmed.[4,5] Bearing in mind that a $CF_3$ group has the properties of a pseudohalide and can be compared with fluorine or chlorine, respectively, it is likely that the structures of all three compounds are similar. It was therefore desirable to determine the crystal structure of $CF_3I(Cl)F$, not only to complete the series of (trifluoromethyl)iodine dihalides but also to study their detailed structures in the solid phase.

## Experimental Section

**CAUTION!** *$CF_3OCl$ is a highly reactive oxidizing agent and potential explosive when brought in contact with organic material. $CF_3I(Cl)F$ is unstable at room temperature and sensitive to moisture. Skin contact with these compounds should be avoided because their hydrolysis leads to HF or HCl, which causes burns and in some cases irreparable damage.*

All synthetic work and sample handling was performed using a standard glass vacuum line and standard Schlenck techniques. Nonvolatile materials were handled under dry nitrogen. The synthesis of (trifluoromethyl)iodine chloride fluoride ($CF_3I(Cl)F$) was carried out by the reaction of trifluoromethyl iodide ($CF_3I$) with (trifluoromethyl) hypochlorite ($CF_3OCl$) at −78 °C based on the literature method.[3] Samples of $CF_3I(Cl)F$ were identified by Raman, infrared, and NMR spectra.

The colorless solid was rapidly crystallized from a mixture of liquid $SO_2$ and $(CH_3)_3SiF$ (ratio 10:1) at −60 °C and stored under dry nitrogen at −70 °C. Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen at about −70 °C, and an X-ray diffraction study at −100 °C was carried out using a Nonius Kappa CCD diffractometer; 360 frames via $\omega$-rotation and 2 times 100 s per frame were measured. The crystal-to-detector distance was 3.1 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Based on an analysis of these duplicate reflections, there was no decay.

$CF_3I(Cl)F$ crystallizes in the orthorhombic system in the space group *Cmca* with $a = 6.898(1)$ Å, $b = 7.310(1)$ Å, $c = 20.127(1)$ Å, and eight formula units per unit cell and is isostructural with $CF_3ICl_2$.[2] The crystal structure was solved by the Patterson method. A search for higher symmetry with the program X-PREP indicated the space group *Cmca* (No. 64). The observed elements of symmetry ($c$-face centered, two axial glide planes, mirror plane) and systematic absences, $(hkl)$ $h + k = 2n + 1$, $(h0l)$ $l = 2n + 1$, and $(hk0)$ $h,k = 2n + 1$, conform to this space group. A final refinement with anisotropic thermal parameters gave values of R1 = 0.0372 and wR2 = 0.0981. For the data reduction, structure solution, and refinement, programs in the SHELXTL package and PARST were used.[6−8] The crystal data are summarized in Table 1.

## Results and Discussion

**Crystal Structure of $CF_3I(Cl)F$.** The molecule has a distorted trigonal bipyramidal structure with the chlorine and fluorine atoms in the apical and the trifluoromethyl group in the equatorial position (Figure 1). This is in accord with the Gillespie−Nyholm model of molecular geometry. The structure can be described as T-shaped and is based on an $AX_3E_2$ arrangement of bond pair and valence electron lone pair domains.[9,10] The same conformation is found for $CF_3IF_2$ and $CF_3ICl_2$.[1,2] Bond lengths and selected angles for $CF_3I(Cl)F$ are summarized in Table 2, and Table 3 contains a comparison of bond lengths, lengths of intermolecular I−Cl and I−F contacts,

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**Table 1.** X-ray Diffraction Data of $CF_3I(Cl)F$

| | |
|---|---|
| space group | *Cmca* (No. 64) |
| *a*, Å | 6.898(1) |
| *b*, Å | 7.310(1) |
| *c*, Å | 20.127(1) |
| vol, Å$^3$ | 1014.9(2) |
| $\rho_{calcd}$, g cm$^{-3}$ | 3.277 |
| *Z* | 8 |
| fw, g mol$^{-1}$ | 250.36 |
| $\mu$, cm$^{-1}$ | 67.99 |
| *T*, °C | −100(2) |
| $\lambda$, Å | 0.71069 |
| $R^a$ [$I > 2\sigma(I)$] | R1 = 0.0372 ,wR2 = 0.0981 |
| $R^a$ (all data) | R1 = 0.0409, wR2 = 0.0999 |
| reflns collected | 2758 |
| indep reflns | 476 [*R*(int) = 0.0400] |
| data/restraints/params | 476/0/41 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on $F^2$.

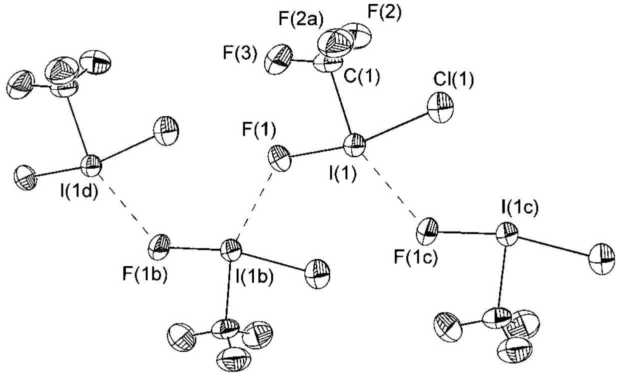

**Figure 1.** Projection of four $CF_3I(Cl)F$ molecules with their intermolecular contacts. The lengths of these contacts are 2.870(6) Å, and the molecules are linked to form chains. The angles formed by these contacts are F(1)−I(1)−F(1d) 119.0(2)° and I(1b)−F(1)−I(1) 130.8(3)°. Symmetry transformations are a = $-x, y, z$; b = $x, {}^1/_2 + y, {}^1/_2 - z$; c = $x, -{}^1/_2 + y, {}^1/_2 - z$; d = $x, -1 + y, z$. Thermal ellipsoids are drawn at the 50% probability level.

**Table 2.** Bond Lengths (Å) and Selected Angles (deg) for $CF_3I(Cl)F^a$

| | | | |
|---|---|---|---|
| I(1)−F(1) | 2.023(6) | F(1)−I(1)−Cl(1) | 167.3(2) |
| I(1)−Cl(1) | 2.412(3) | Cl(1)−I(1)−C(1) | 83.0(3) |
| I(1)−C(1) | 2.197(11) | F(1)−I(1)−C(1) | 84.2(4) |
| F(2)−C(1) | 1.304(9) | F(2)−C(1)−I(1) | 109.4(6) |
| F(2a)−C(1) | 1.304(9) | F(2a)−C(1)−I(1) | 109.4(6) |
| F(3)−C(1) | 1.305(15) | F(3)−C(1)−I(1) | 110.6(7) |
| | | F(2)−C(1)−F(2a) | 109.8(9) |
| | | F(2)−C(1)−F(3) | 108.8(7) |
| | | F(2a)−C(1)−F(3) | 108.8(7) |

[a] Symmetry transformation used to generate equivalent atoms: a = $1 - x, y, z$.

**Table 3.** Crystallographic and Structural Data for the (Trifluoromethyl)iodine Dihalides

| | $CF_3IF_2$ [1] | $CF_3I(Cl)F$ | $CF_3ICl_2$ [2] |
|---|---|---|---|
| I−Cl bond length (Å) | | 2.412(3) | 2.478(2)<br>2.457(2) |
| I−F bond length (Å) | 1.982(2)<br>1.982(2) | 2.023(6) | |
| X−I−Y angle (deg) | 165.4(2) | 167.3(2) | 171.62(9) |
| intermolecular I−F contact (Å) | 2.950(2) | 2.870(6) | |
| intermolecular I−Cl contact (Å) | | | 3.324(3) |

and selected Cl−I−Cl angles for the three known (trifluoromethyl)iodine dihalides. The axial bonds in the iodine(III) compounds may be described as 3-center-4-electron bonds, and thus bond lengths are very difficult to predict. Varvoglis reported that, in iodine(III) compounds where the axial ligands have the same electronegativity, the bonds between these ligands and iodine are longer than the sum of their covalent radii.[11] When the ligands are of different electronegativities, the distance between iodine and the less electronegative ligand is comparable to the sum of the covalent radii, while the bond to the more electronegative ligand is longer than the covalent radii.[11] This effect increases with increasing differences in electronegativity and size.[12]

In $CF_3I(Cl)F$ the I−Cl bond has a length of 2.412(3) Å and is significantly shorter than those in $CF_3ICl_2$ with 2.457(2) and 2.478(2) Å. Bearing in mind the model of bonding described by Varvoglis, it is not surprising that the I−F bond length of 2.023(6) Å is significantly longer than in $CF_3IF_2$ (1.982(2) Å) and is longer than the sum of the covalent radii of 1.92 Å, published by Bondi.[1,13] The structure of $CF_3I(Cl)F$ is isostructural with that of $CF_3ICl_2$.[2] The only differences occur in the secondary bonding. In $CF_3ICl_2$, the molecules exhibit donor−acceptor properties by forming two intermolecular I−Cl contacts of 3.323(3) Å that result in a distorted square planar environment around iodine. The crystal structure of $CF_3I(Cl)F$ has a similar arrangement, but only involves I−F contacts. These contacts, with a length of 2.870(6) Å, result in the formation of chains (Figure 1). The $CF_3$ group exhibits no intermolecular contacts and occupies the position of a side group of the chains. A completely different linkage is found in $CF_3IF_2$.[1] Each $CF_3IF_2$ molecule has contacts to four adjacent molecules. Two contacts are made by the apical fluorines, and the others are made by the iodine, to give a distorted pentagonal arrangement for the iodine. The lengths of all these contacts are 2.950(2) Å, and they result in zigzag chains.[1] A similar secondary bond linkage is found for $XeF_3^+ SbF_6^-$.[14] In its crystal structure there are two interionic Xe−F contacts with lengths of 2.485(10) and 2.715(13) Å, coplanar to the three fluorine ligands, resulting in a distorted pentagonal planar environment for xenon. This is due to the tendency of the incoming lone pairs to avoid the domains of the other electrons in the valency shell of xenon.[14] In all these compounds the two apical ligands are bent toward the equatorial ligand due to the higher space requirement of the two lone pair domains. With this information, we think it is possible to predict the structures of $ICl_2F$ and $IF_2Cl$. In our opinion, both molecules will be monomers in the solid state, but with strong intermolecular interactions, and $IF_2Cl$ will be similar to $CF_3IF_2$, i.e., the fluorines occupy the apical positions in the trigonal bipyramid with I−F bond lengths close to 1.98 Å. The I−Cl bond length is expected to be in the range of 2.35−2.40 Å, comparable to the terminal bonds in $I_2Cl_6$ of 2.38 and 2.39 Å.[15] The intermolecular contacts will be similar to those in $CF_3IF_2$. For $ICl_2F$, we expect a structure with fluorine in an apical position and bond lengths similar to those found in $CF_3I(Cl)F$. These predictions are supported by comparison with the structurally known (trifluoromethyl)iodine(III) compounds in which the equatorial positions are always occupied by two lone pairs and a $CF_3$ group.[1,2,12,16] The C−I bonds have lengths of nearly 2.20 Å and can be described as normal single bonds.

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The hypervalent behavior of iodine has the greatest influence on the apical positions, which are bent by the 5p$_z$ orbital of iodine by electron-deficient bonds. Thus the structures of (trifluoromethyl)iodine(III) compounds are mainly determined by the groups occupying the apical positions, enabling one to predict the structures of iodine(III) derivatives whose structures are still not known.

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**Supporting Information Available:** One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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