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A New Method for Preparation and Crystal Structure of (Trifluoromethyl)iodine Dichloride

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(Trifluoromethyl)iodine dichloride (CF_3ICl_2) is synthesized by the reaction of (trifluoromethyl)iodine chloride fluoride ($CF_3I(Cl)F$) with trimethylchlorosilane ($((CH_3)_3SiCl)$) at −40 °C. By using this route of preparation, in which $CF_3I(Cl)F$ undergoes a chlorine−fluorine exchange, CF_3ICl_2 can be obtained in high purity and yield. CF_3ICl_2 crystallizes in the orthorhombic space group *Cmca* with $a = 6.990(1)$ Å, $b = 7.985(1)$ Å, $c = 21.177(1)$ Å, and eight formula units per unit cell. The final R indices $[I > 2\sigma(I)]$ are $R_1 = 0.0341$ and $wR_2 = 0.0631$. CF_3ICl_2 is, in contrast to iodine trichloride (ICl_3), monomeric, and its molecular structure is T-shaped with the CF_3 group in the equatorial position. The Raman, IR, and NMR spectra are also described.

Introduction

After we recently reported a new preparation and the crystal structure of (trifluoromethyl)iodine difluoride (CF_3IF_2), we now present a new route of preparation of (trifluoromethyl)iodine dichloride (CF_3ICl_2) and its crystal structure.[1]

The first spectroscopic indication for the existence of CF_3ICl_2 was found in 1976 by Naumann et al. in a study of the reaction of trifluoromethyl iodide (CF_3I) with chlorine nitrate ($ClONO_2$).[2] In this reaction (trifluoromethyl)iodine chloride nitrate ($CF_3I(Cl)ONO_2$) was found to be an intermediate in the preparation of (trifluoromethyl)iodine dinitrate ($CF_3I(ONO_2)_2$). $CF_3I(Cl)ONO_2$ was not isolated, because it was thought to be in equilibrium with CF_3ICl_2 and $CF_3I(ONO_2)_2$.

The CF_3ICl_2 could not be isolated, and only a ^{19}F NMR value for the CF_3 group was given. Three years later in his dissertation Reinelt described the preparation and isolation of CF_3ICl_2 by the reaction of CF_3IF_2 and tetrachlorosilane ($SiCl_4$) at −50 °C in $CFCl_3$.[3] CF_3ICl_2 was characterized by its Raman and ^{19}F NMR spectra. The reaction of CF_3I with chlorine (Cl_2), analogous to the preparation of CF_3IF_2 by direct fluorination of CF_3I, was described to yield CF_3ICl_2 in only small amounts.[3]

In 1989 Tyrra and Naumann published the preparation of CF_3ICl_2 by the reaction of CF_3IF_2 with $SiCl_4$ or $(CH_3)_3SiCl$.[4] The resulting CF_3ICl_2 was characterized by ^{19}F NMR spectroscopy and was used as a starting material for substitution reactions with different silver salts to yield new (trifluoromethyl)iodine (III) compounds.

Two years later the third and up to now last report on CF_3ICl_2 was published also by Tyrra and Naumann. In this publication, CF_3ICl_2 was prepared by trifluoromethylating iodine trichloride (ICl_3) with, for example, bis(trifluoromethyl)cadmium ($Cd(CF_3)_2$) or mercury compounds.[5]

CF_3ICl_2 can be considered as a trifluoromethyl-substituted derivative of ICl_3. Since in the solid state ICl_3 exists only as a dimer, it was interesting to determine what influence the substitution of one chlorine ligand by a CF_3 group has.[6] In the case of $C_6H_5ICl_2$, the crystal structure has shown that the C_6H_5 group prevents dimerization.[7]

Since there is great interest in the crystal structures of iodine(III) compounds and especially of trifluoromethyl-substituted ones, it was desirable to determine the crystal structure of CF_3ICl_2.

Experimental Section

Caution! CF_3OCl is a highly reactive oxidizing agent and potentially explosive when brought in contact with organic material. $CF_3I(Cl)F$ and CF_3ICl_2 are unstable at room temperature. Skin contact with these compounds should be avoided because their hydrolysis leads to HF, HCl, or Cl_2, which causes burns and in some cases irreparable damage.

All synthetic work and sample handling were 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 CF_3I with trifluoromethyl hypochlorite (CF_3OCl) at −78 °C based on the literature method.[8] Trimethylchlorosilane ($((CH_3)_3SiCl)$) was distilled before using to avoid the presence of hexamethyldisiloxane ($((CH_3)_3SiOSi(CH_3)_3)$).

Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra of dry powders were obtained in a low-temperature cell with CsBr plates coated with the pure sample.[9] Raman spectra were recorded on a Jobin Yvon T64000 spectrometer by using an Ar^+ laser (514.5 nm, Spectra Physics). The spectra were recorded in glass cells cooled with liquid nitrogen or solid CO_2.[10] Single crystals were placed in Lindemann capillaries in a cooled stream of dry nitrogen, and an X-ray diffraction study was carried out by using a Nonius Kappa CCD diffractometer. The NMR spectra were obtained in SO_2 at −40 °C on a Bruker DPX 300 and a Bruker DRX 400 with $CFCl_3$ (^{19}F) or $(CH_3)_4Si$ (^{13}C) as external standards.

Preparation of CF_3ICl_2. $(CH_3)_3SiCl$ (0.24 g, 2.2 mmol) was condensed into a dry glass vessel with greaseless stopcocks (Young) onto 0.5 g (2 mmol) of $CF_3I(Cl)F$. The mixture was allowed to warm to −40 °C and was held at this temperature over a period of 1 h. After

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[1] Minkwitz, R.; Berkei, M. *Inorg. Chem.* **1998**, *37*, 5247.

[2] Naumann, D.; Heinsen, H. H.; Lehmann, E. *J. Fluorine Chem.* **1976**, *8*, 243.

[3] Reinelt, P., Dissertation, University of Dortmund, Germany, 1979.

[4] Naumann, D.; Tyrra, W. *J. Fluorine Chem.* **1989**, *45*, 401.

[5] Tyrra, W.; Naumann, D. *Can. J. Chem.* **1991**, *69*, 327.

[6] Boswijk, K. H.; Wiebenga, E. H. *Acta Crystallogr.* **1954**, *7*, 417.

[7] Archer, E. M.; Van Schalwyk, T. G. D. *Acta Crystallogr.* **1953**, *6*, 88.

[8] Minkwitz, R.; Bröchler, R.; Schütze, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1727.

[9] Bayersdorfer, L.; Minkwitz, R.; Jander, J. *Z. Anorg. Allg. Chem.* **1972**, *392*, 137.

[10] Werner, A., Dissertation, University of Dortmund, Germany, 1988.

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the volatile materials were removed under vacuum at −40 °C, the formation of CF_3ICl_2 was observed. The resulting pale yellow solid is stable up to −35 °C and sensitive to moisture. The solid was recrystallized from liquid SO_2 at −50 °C and stored under dry nitrogen at −70 °C.

Results and Discussion

Reaction of $CF_3I(Cl)F$ with $(CH_3)_3SiCl$. Since $CF_3I(Cl)F$ can easily be obtained by the reaction of CF_3I with CF_3OCl at −78 °C, it is a good starting material for the preparation of different iodine(III) compounds. The reaction between $CF_3I(Cl)F$ and $(CH_3)_3SiCl$ is simple and efficient. It is almost quantitative, and no side products, except for $(CH_3)_3SiF$, appear. The driving force for this reaction is the formation of the Si−F bond (D_o = 565 kJ/mol) replacing the Si−Cl bond (D_o = 381 kJ/mol).[11] Because of this, the reaction can be carried out at mild reaction conditions, and it opens up a general way to obtain the usually temperature unstable trifluoromethyl-substituted iodine(III) compounds. The oxidative addition of CF_3I with Cl_2 is not successful and yields CF_3ICl_2 in only small amounts.[3]

It seems that the equilibrium which is shown in (1) is essentially on the side of the starting materials. This equilibrium

$$CF_3I + Cl_2 \rightleftarrows CF_3ICl_2 \qquad (1)$$

can be shifted to the favor of CF_3ICl_2 by using liquid Cl_2 in a great excess and a Hg lamp.[3] Under these conditions, pure CF_3ICl_2 can be obtained at −78 °C in low yields. Apparently, using $CF_3I(Cl)F$ as the starting material for the preparation of CF_3ICl_2 is not the shortest but the most efficient way, because of the high yield and less preparative expense.

Crystal Structure of CF_3ICl_2. CF_3ICl_2 crystallizes in the orthorhombic space group *Cmca* with a = 6.990(1) Å, b = 7.985(1) Å, c = 21.177(1) Å, and eight formula units per unit cell. The crystal structure was solved by direct methods. A search for higher symmetry with the program X-PREP indicated the space groups *Cmca* (no. 64) and *Aba*2 (no. 41). The observed elements of symmetry (*c*-face centered, two axial glide planes, mirror plane) and systematic absences, (hkl) $h + k = 2n + 1$ and ($hk0$) h, $k = 2n + 1$, conform to the space group *Cmca*. A final refinement with anisotropic thermal parameters gave values of R_1 = 0.0341 and wR_2 = 0.0631. For the data reduction, structure solution and refinement, programs in the SHELXTL package and PARST were used.[12−14] The crystal data are summarized in Table 1.

Table 1. X-ray Diffraction Data of CF_3ICl_2

space group	*Cmca* (no. 64)	μ, cm^{-1}	62.62
a, Å	6.990(1)	T, °C	−100(2)
b, Å	7.985(1)	λ, Å	0.710 69
c, Å	21.177(1)	R^a [$I > 2\sigma(I)$]	R_1 = 0.0341, wR_2 = 0.0631
volume, Å^3	1182.0(2)		
ρ_{calcd}, g cm^{-3}	2.999	R^a (all data)	R_1 = 0.0554, wR_2 = 0.1151
Z	8		
fw	266.81		

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

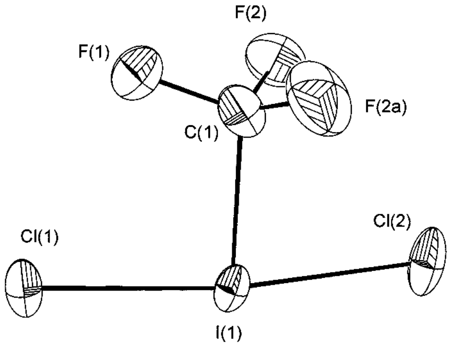

Figure 1. Projection of the CF_3ICl_2 molecule. The symmetry transformation to generate equivalent atoms is $a = 1 - x, y, z$. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Bond Lengths (Å) and Selected Angles (deg) for CF_3ICl_2[a]

I(1)−Cl(1)	2.478(2)	Cl(1)−I(1)−Cl(2)	171.62(9)
I(1)−Cl(2)	2.457(2)	Cl(1)−I(1)−C(1)	88.7(3)
I(1)−C(1)	2.229(10)	Cl(2)−I(1)−C(1)	82.9(3)
F(1)−C(1)	1.303(10)	F(1)−C(1)−I(1)	109.9(6)
F(2)−C(1)	1.299(7)	F(2)−C(1)−I(1)	107.9(6)
F(2a)−C(1)	1.299(7)	F(2a)−C(1)−I(1)	107.9(6)
		F(1)−C(1)−F(2)	110.0(6)
		F(1)−C(1)−F(2a)	110.0(6)
		F(2)−C(1)−F(2a)	111.1(8)

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

Table 3. I−Cl Bond Lengths (Å), Lengths of Intermolecular I−Cl Contacts, and Selected I−Cl_2 Angles (deg) for Different Molecules

molecule	I−Cl bond length	I···Cl contact length	I−Cl_2 angle
I_2Cl_6[6]	2.38	3.55	172
	2.39	3.57	
	2.68 (bridging)	3.60	
	2.72 (bridging)		
CF_3ICl_2	2.478(2)	3.324(3)	171.62(9)
	2.457(2)		
$C_6H_5ICl_2$[7]	2.450(15)	3.40	not available[a]
TripICl_2[b,22]	2.457(2)	3.490(2)	176.8(1)
	2.530(1)		

[a] No concrete value given by the authors. [b] Trip = 2,4,6-*i*-$Pr_3C_6H_2$.

The molecule has a distorted trigonal bipyramidal structure with the two chlorine atoms in the apical and the trifluoromethyl group in the equatorial positions (Figure 1). This is in accordance with the Gillespie−Nyholm model, and the structure can be described as T-shaped.[15,16] The same conformation is found for CF_3IF_2, $C_6H_5ICl_2$, ClF_3, and BrF_3.[1,7,17,18] Bond lengths and selected angles for CF_3ICl_2 are summarized in Table 2, and Table 3 contains a comparison of I−Cl bond lengths, lengths of intermolecular I−Cl contacts, and selected Cl−I−Cl angles for different molecules. The axial I−Cl bonds in CF_3ICl_2 are three-center-four-electron semiionic bonds and have lengths of 2.478(2) and 2.457(2) Å. The angle between the iodine and the two apical chlorines is 171.62(9)°, and the chlorine atoms are bent toward the CF_3 group, due to the higher space requirement of the two lone pairs. These values are in the normal range for iodine(III) compounds containing chlorine as a ligand and can be compared to those in $C_6H_5ICl_2$ (2.450(15) Å)[7] and ICl_4^- (2.42−2.60 Å)[19] and the terminal bonds in the dimeric I_2Cl_6

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(11) Huheey, J. E. *Anorganische Chemie*; Walter de Gruyter: Berlin, New York, 1988.

(12) Sheldrick, G. M. SHELXTL PLUS, An Integrated System for Solving, Refining and Displaying Structures from Diffraction Data, University of Göttingen, Germany, 1987.

(13) Nardelli, M. *Comput. Chem.* **1986**, *7*, 95.

(14) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132652 (CF_3ICl_2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, U.K. (Fax +44−1223/336−033, e-mail deposit@ccdc.cam.ac.uk).

(15) Gillespie, R. J.; Nyholm, R. S. *Q. Rev. Chem. Soc.* **1957**, *11*, 339.

(16) Gillespie, R. N. *J. Chem. Educ.* **1963**, *40*, 295.

(17) Burbank, R. D.; Bensey, F. N. *J. Chem. Phys.* **1953**, *21*, 602.

(18) Burbank, R. D.; Bensey, F. N. *J. Chem. Phys.* **1957**, *27*, 982.

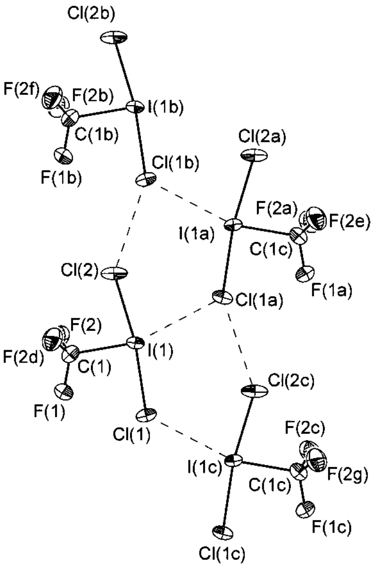

Figure 2. Projection of four CF_3ICl_2 molecules with their intermolecular contacts. The contacts result in chains of five-membered rings linked by one side. The lengths of these contacts are 3.324(3) Å for I−Cl and 3.361(3) Å for Cl−Cl. The angles formed by these contacts are Cl(2)−Cl(1b)−I(1a) = 81.08(7)°, Cl(1b)−I(1a)−Cl(1a) = 109.15(7)°, I(1a)−Cl(1a)−I(1) = 126.15(9)°, Cl(1a)−I(1)−Cl(2) = 79.23(8)°, and I(1)−Cl(2)−Cl(1b) = 144.40(13)°. Symmetry transformations are $a = x, -1/2 + y, 3/2 - z$; $b = x, 1 - y, z$; $c = x, 1/2 + y, 3/2 + z$; $d = 1 - x, y, z$; $e = 1 - x, -1/2 + y, 3/2 - z$; $f = 1 - x, -1 + y, z$; and $g = 1 - x, 1/2 + y, 3/2 - z$. Thermal ellipsoids are drawn at the 50% probability level.

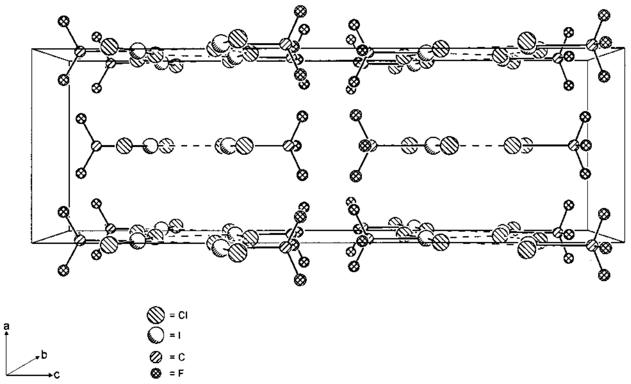

Figure 3. View of the unit cell in the *b*-orientation. The molecules are arranged in layers parallel to the *b*−*c* plane.

Table 4. Raman and IR Frequencies of CF_3ICl_2

Raman (T = −196 °C)	Raman[3] (T = −100 °C)	IR (T = −40 °C)	assignment
		1705 (vw)	$\delta_s(CF_3) + \nu_s(CF_3)$
1245 (0.1)		1277 (w)	$\nu_{as}(CF_3)$
1226 (0.1)		1220 (vs)	$\nu_{as}(CF_3)$
1059 (0.3)	1054 (0.3)	1024 (m)	$\nu_s(CF_3)$
		991 (m)	impurity?
750 (0.6)	745 (0.9)	739 (m)	$\delta_s(CF_3)$
		546 (vw)	$\delta_{as}(CF_3)$
292 (10.0)	288 (10.0)	291 (vs)	$\nu_s(ICl_2)$
279 (1.1)	275 (0.9)	278 (vs)	$\nu(CI)$
265 (1.9)	262 (2.4)	262 (vs)	$\nu_{as}(ICl_2)$
247 (2.9)	244 (2.6)		$\rho(CF_3)$
163 (0.5)	160 (0.6)		$\gamma(ICl_2)$
154 (0.3)			impurity?
145 (0.9)	141 (1.0)		$\delta(ICl_2)$
92 (1.1)	89 (1.4)		lattice modes
72 (0.4)	65 (0.4)		lattice modes
	41 (2.4)		lattice modes

(2.38 and 2.39 Å).[6] This is not surprising, because the main difference between various iodine(III) chlorides is their formation of secondary bonds. Besides the three bonds between iodine and the two chlorines and the third ligand, there is usually a secondary bond between iodine and a chlorine atom of an adjacent molecule. In the case of ICl_3, two ICl_3 units are double bridged to each other, and these bridges are so strong that the molecule exists only as dimers.[6] Table 3 shows that the strength of the I−Cl bridges decreases with increasing bulkiness of the third ligand. In the case of ICl_3 the third ligand is a chlorine as well. Because of this, the molecule is able to form two pairs of equal bonds, two terminal and two bridging, to reach a nearly square planar environment of iodine such as in ICl_4^-.[6,19] Keeping this in mind, it is clear that the bridging bonds will be longer than the terminal bonds. They can be described as three-center−four-electron bonds with one electron pair in a binding orbital and the other one in a nonbinding orbital. The nearly square planar environment of iodine in ICl_3 is forced by the two lone pairs, which take the axial positions, and a distorted octahedral results. In CF_3ICl_2 the two lone pairs at the iodine press the chlorine atoms in the axial positions toward the bulky CF_3 group. The intermolecular contact in CF_3ICl_2 has a length of 3.324 Å and is much longer than the bridging bonds in I_2Cl_6 (2.68−2.72 Å), but obviously shorter than in $C_6H_5ICl_2$ (3.40 Å) and 2,4,6-*i*-$Pr_3C_6H_2ICl_2$ (3.49 Å).[6,7,20]

In addition to the I−Cl contacts, CF_3ICl_2 also contains weak Cl−Cl contacts of 3.361 Å, 4% under the sum of the van der Waals radii (3.5 Å), which are due to packing effects.[21] All these contacts result in the formation of chains of side-linked five-membered rings (Figure 2). The CF_3 group undergoes no intermolecular contacts and occupies the position of a side group of the chains.

As shown in Figure 3 the molecules are arranged in layers stacked parallel to the *a* axis. The minimum distance between a chlorine and an iodine between different layers is 3.838 Å (the sum of the van der Waals radii published by Bondi is 3.73 Å), indicating no significant interaction between the layers.[21]

The C−I distance of 2.229(10) Å is comparable to those in similar compounds such as CF_3IF_2 (2.174(6) Å),[1] CF_3IF_4 (2.22(1) Å),[22] or $CF_3I(ONO_2)_2$ (2.212(4) Å).[23] The CF_3 group is, as expected, nearly tetrahedral with F−C−F angles of 110.0(6)° and 111.1(8)° and C−F bond lengths of 1.299(7) and 1.303(10) Å.

Vibrational Spectra. As shown by its crystal structure, isolated CF_3ICl_2 has C_s symmetry with 15 fundamental vibrations, which are all Raman and IR active. As in the case of CF_3IF_2 for CF_3ICl_2, the eclipsed conformation is found, and our assignments are made on this basis. In this conformation there are 10 vibrations in A′ and 5 in A″. This is due to $\nu_{as}(ICl_2)$, which is only in the eclipsed conformation in the A′ mode. The frequencies and assignments are listed in Table 4 in comparison to those obtained by Reinelt.[3] Figure 4 shows the vibrational spectra.

The ICl_2 stretching modes are observed at 292 and 265 cm^{-1} for the symmetric and antisymmetric stretches of (ICl_2), respectively. This assignment was verified by Reinelt, who was able to record resonance Raman spectra of CF_3ICl_2 solutions

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(19) Elema, R. J.; De Boer, J. L.; Vos, A. *Acta Crystallogr.* **1963**, *16*, 243.

(20) Mishra, A. K.; Olmstead, M.; Ellison, J. J.; Power, P. P. *Inorg. Chem.* **1995**, *34*, 3210.

(21) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(22) Minkwitz, R.; Bröchler, R.; Preut, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1247.

(23) Minkwitz, R.; Hertel, T. *Z. Anorg. Allg. Chem.* **1997**, *623*, 659.

Figure 4. Raman and IR spectra of CF_3ICl_2.

in CH_3CN.[3] The ICl_2 bending modes are at 160 cm^{-1} for γ (ICl_2) and at 145 cm^{-1} for δ(ICl_2).

The C−I stretching mode is found at 279 cm^{-1} and is comparable to other trifluoromethyl-substituted iodine(III) compounds as CF_3IF_2 (281 cm^{-1}) or $CF_3I(Cl)F$ (275 cm^{-1}).[1,8] Since the C−I stretching mode and the antisymmetric stretching of ICl_2 are found in the same range with similar intensities, the reverse assignment for these vibrations is also possible. The CF_3 group vibrations are also in the expected range. The stretching vibrations are found between 1024 and 1277 cm^{-1}, and the symmetric bending mode, $\delta_s(CF_3)$, is detected at 750 cm^{-1} in the Raman spectrum and at 739 cm^{-1} in the IR spectrum. The antisymmetric CF_3 bending mode was observed only in the IR spectrum at 546 cm^{-1} because of its low Raman activity. The assignment of the CF_3 rocking mode is difficult, because it is expected in the same range as $\nu_{as}(ICl_2)$. We have assigned it to the line at 247 cm^{-1} and, as described above, the antisymmetric stretching mode of ICl_2 to the line at 265 cm^{-1}, but the reverse assignment is also possible.

NMR Spectra. The resonance at −28.99 ppm in the ^{19}F NMR spectrum can be assigned to the CF_3 group and is in accordance with the value published by Naumannn et al.[2] Literature data for similar iodine(III) compounds are in the range between −33.7 ppm (CF_3IF_2) and −25.4 ppm ($CF_3I(OCOCF_3)_2$).[24,25]

In the ^{13}C NMR spectrum the signal for the CF_3 group is recorded at 91.9 ppm with $^1J(C-F)$ of 365 Hz. For CF_3I a value of 78.2 ppm with $^1J(C-F)$ of 344 Hz and for $(CH_3)_4N^+CF_3ICl^-$ a value of 84.6 ppm with $^1J(C-F)$ of 350 Hz were published.[26,27]

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Supporting Information Available: A CIF file and tables listing crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Baumanns, J.; Deneken, L.; Naumann, D.; Schmeisser, M. *J. Fluorine Chem.* **1973**, *3*, 323.
(25) Naumann, D.; Baumanns, J. *J. Fluorine Chem.* **1976**, *8*, 177.
(26) De Marco, R. A.; Fox, W. B.; Moniz, W. B.; Sojka, S. A. *J. Magn. Reson.* **1975**, *18*, 522.
(27) Minkwitz, R.; Bröchler, R.; Berkei, M. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1749.