An Accidental Discovery of a New Mixed-Valent Iodine Compound − Crystal Structure of Difluoroiodato(V) Iodine(III) Dichloride [$Cl_2IOI(O)F_2$]

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The crystal structure of the novel iodine compound $Cl_2IOI(O)F_2$ is described. $Cl_2IOI(O)F_2$ contains iodine in two different oxidation states (III) and (V) and can formally be described as $ICl_2^+IF_2O_2^-$, linked by an unsymmetrical, non-linear I–O–I bridge, with I–O bond lengths of 1.84(1) Å and 2.32(1) Å, and a bond angle of 122.5(5)°. It was accidentally obtained by the uncontrolled reaction between CF_3I, CF_3OCl, CF_2O, and Cl_2 at –70 °C over a period of about six months and finally two days at room temperature. $Cl_2IOI(O)F_2$ crystallises in the monoclinic space group $P2_1/c$ with four formula units per unit cell with the dimensions $a = 12.910(1)$, $b = 6.987(1)$, $c = 7.550(1)$ Å, and $\beta = 94.890(1)$°. The molecule was additionally characterised by its Raman and IR spectra.

Introduction

Compounds containing iodine in different oxidation states are rather rare, and in most cases limited to polyiodide anions and cations. In neutral compounds, comproportionation to give the more stable oxidation state often takes place. An example of a stable mixed-valent iodine compound is $I(OSO_2F)_2I$.[1] It formally contains an iodine(III) and an iodide(−I). The I−I bond has a length of 2.676(1) Å and shows no ionic character, as might be expected.[1] Another example was reported by Kraft and Jansen in 1996.[2] The authors described the synthesis and characterisation of iodine trioxide I_4O_{12} which contains iodine in the oxidation states (V) and (VII).[2] In 1992, Rehr and Jansen determined the crystal structure of $(IO_2)_3HSO_4$ and reported a complex iodoxo polycation with iodine(III) and (V).[3] It seems that oxygen stabilises these compounds by secondary bonding, so that the tendency to comproportionation becomes negligible.

In this work we report the accidental preparation and crystal structure of difluoroiodato(V) iodine(III) dichloride [$Cl_2IOI(O)F_2$], a singular example of an iodine oxofluoride chloride with mixed-valent iodine atoms.

Results and Discussion

Formation of $Cl_2IOI(O)F_2$

$Cl_2IOI(O)F_2$ was accidentally obtained by the uncontrolled reaction between CF_3I, CF_3OCl, CF_2O, and Cl_2. These compounds were stored in a closed Pyrex ampoule at −70 °C over a period of about six months. After this time the formation of a yellow-orange solid beneath a yellow liquid was observed. The solid was thought to be I_2Cl_6 and so the ampoule was broken and introduced into an outlet at room temperature. Two days later, orange and red crystals were observed in the ampoule, which also contained a yellow gas. The ampoule was then stored under nitrogen at −70 °C, because on exposure to air the crystals were observed to decompose.

All solids were characterised by single crystal X-ray diffraction. The red solid was identified as α-ICl and the orange one as a mixture of I_2Cl_6 and $Cl_2IOI(O)F_2$. We think that the formation of $Cl_2IOI(O)F_2$ involves a complex mechanism, which is still unknown. Bearing in mind that the reaction between CF_3I and excess CF_3OCl yields IF_5, it is likely that IF_5 or a related iodine(V) oxofluoride is one possible intermediate in the formation of $Cl_2IOI(O)F_2$.[4−6] Attempts to repeat the synthesis of $Cl_2IOI(O)F_2$ failed. We decided to try to obtain an X-ray crystal structure and measure the Raman and IR spectra first, and used all the available material. Because of the small quantity of $Cl_2IOI(O)F_2$ obtained we were not able to perform further investigations.

Crystal Structure of $Cl_2IOI(O)F_2$

$Cl_2IOI(O)F_2$ crystallises in the monoclinic system in the space group $P2_1/c$ with $a = 12.910(1)$ Å, $b = 6.987(1)$ Å, $c = 7.550(1)$ Å, $\beta = 94.890(1)$°, and four formula units per unit cell. The crystal structure was solved by direct methods and successive difference Fourier syntheses. For refinement full-matrix least-squares methods were applied. A final refinement with anisotropic thermal parameters gave values of $R1 = 0.0558$ and $wR2 = 0.1297$. For the data reduction, structure solution, and refinement, programs in the SHELXTL package, PLATON, MISSYM, and PARST were used.[7−11] The crystal data are summarised in Table 1.

$Cl_2IOI(O)F_2$ can be described as two pseudo-trigonal bipyramids linked by one edge over an unsymmetrical I−O−I bridge with lengths of I(1)−O(1) 1.84(1) Å, I(2)−O(1) 2.32(1) Å and an angle I(1)−O(1)−I(2) of 122.5(5)° (Figure 1). The bridging I(2)−O(1) bond is about 20% longer than the sum of the covalent radii (1.94 Å) and

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Table 1. X-ray diffraction data of $Cl_2IOI(O)F_2$

Space group	$P2_1/c$
Crystal system	monoclinic
a, Å	12.910(1)
b, Å	6.987(1)
c, Å	7.550(1)
α, °	90
β, °	94.89(1)
γ, °	90
Volume, Å^3	678.6(1)
Density (calculated), g cm^{-3}	3.864
Z	4
Formula weight, g mol^{-1}	394.70
Absorption coefficient, mm^{-1}	10.012
Temperature, K	173(2)
F(000)	696
Wavelength, Å	0.71069
Theta range for data collection, °	$3.32 \leq \theta \leq 25.68$
Index ranges	$-14 \leq h \leq 13$, $-7 \leq k \leq 7$, $-6 \leq l \leq 8$
Reflections collected/independent	3309/1071 [$R(int) = 0.0818$]
Parameters	74
Goodness-of-fit on F^2	1.201
Final R indices [$I < 2\sigma(I)$]	$R1 = 0.0558$, $wR2 = 0.1297$
R indices (all data)	$R1 = 0.0725$, $wR2 = 0.1557$
Largest diff. peak and hole, e. Å^{-3}	1.685 and −2.066
Refinement method	full matrix, least-squares on F^2

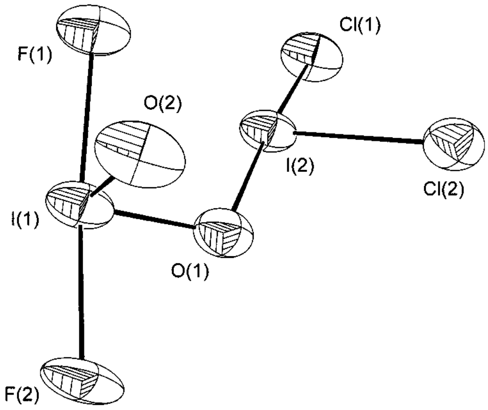

Figure 1. View of a $Cl_2IOI(O)F_2$ molecule; thermal ellipsoids are drawn at the 50% level

34% below the sum of the van der Waals radii (3.50 Å), as published by Bondi.[12] This secondary bond results in a distorted square planar environment around iodine.[13] We think that this description for $Cl_2IOI(O)F_2$ is more reasonable than formulating it as $ICl_2{}^+IO_2F_2{}^-$. The molecule contains iodine in two different oxidation states (III) and (V). The axial positions in the iodine(V) group are occupied by fluorine and the equatorial ones by a lone pair, a double bond oxygen, and the bridging oxygen.[14] In agreement with the Gillespie-Nyholm model of molecular geometry, the iodine(III) unit contains chlorine and oxygen in the apical positions, and one chlorine and two lone pairs in the equatorial plane.[15,16] Bond lengths and selected angles for $Cl_2IOI(O)F_2$ are listed in Table 2.

Table 2. Bond lengths [Å] and angles [°] of $Cl_2IOI(O)F_2$ and lengths [Å] and angles [°] of selected intermolecular contacts[a]

I(1)−O(1)	1.84(1)	O(1)−I(1)−O(2)	100.7(5)
I(1)−O(2)	1.81(1)	O(1)−I(1)−F(1)	90.1(4)
I(1)−F(1)	1.969(8)	O(1)−I(1)−F(2)	88.6(5)
I(1)−F(2)	1.917(8)	O(2)−I(1)−F(1)	85.2(4)
I(2)−Cl(1)	2.343(4)	O(2)−I(1)−F(2)	87.4(4)
I(2)−Cl(2)	2.352(5)	F(1)−I(1)−F(2)	172.2(4)
I(2)−O(1)	2.32(1)	Cl(1)−I(2)−Cl(2)	94.1(2)
		O(1)−I(1)−Cl(1)	175.5(3)
I(1)···F(1a)	3.038(8)	O(1)−I(1)−Cl(2)	84.2(3)
I(1)···F(1b)	3.259(9)	I(1)−O(1)−I(2)	122.5(5)
I(1)···F(2c)	3.10(1)		
I(1)···O(2a)	3.32(1)	O(1)−I(1)−O(2d)	170.0(4)
I(1)···O(2d)	2.77(1)	O(2)−I(1)−O(2a)	144.4(4)
I(2)···O(1a)	3.36(1)	O(2)−I(1)−F(1a)	167.3(4)
I(2)···O(2a)	2.50(1)	O(2)−I(1)−F(1b)	117.7(4)
		O(2)−I(1)−F(2c)	115.9(5)
		Cl(2)−I(2)−O(1a)	127.1(2)
		Cl(2)−I(2)−O(2a)	166.0(3)

[a] Symmetry transformations: *a*: x, $1/2 - y$, $-1/2 + z$; *b*: $1 - x$, $1/2 + y$, $1/2 - z$; *c*: $1 - x$, $-1/2 + y$, $1/2 - z$; *d*: $1 - x$, $1 - y$, $1 - z$; *e*: x, $1/2 - y$, $1/2 + z$.

The I−F bonds have lengths of 1.969(8) and 1.917(8) Å and are comparable to those found in IF_3O [1.91(3) and 1.89(3) Å] and in $IF_2(O)OCH_3$ [1.929(3) and 1.964(3) Å].[17,18] The angle between iodine and the two fluorine atoms is 172.2(4)° and shows a difference from the ideal value of 180° due to the steric activity of the lone pair. In $Cl_2IOI(O)F_2$ there is an axial as well as an equatorial I−Cl bond, whose lengths of 2.343(4) and 2.352(5) Å are only slightly larger than the sum of the covalent radii (2.27 Å).[12] The I(2)−O(1) bond, with oxygen as the most electronegative ligand of I(2), has a length of 2.32 (1) Å and is significantly longer than the sum of the covalent radii of 1.94 Å, as published by Bondi.[12] This is in agreement with the principle reported by Varvoglis that, in iodine(III) compounds with axial ligands of different electronegativities, the distance between iodine and the more electronegative ligand is longer than the sum of the covalent radii, while the bond to the less electronegative ligand is comparable with the sum of covalent radii.[19] The bridging angle I(1)−O(1)−I(2) [122.5(5)°] is similar to those found in I_4O_{12} [102.1(4)−129.2(4)°] and $(IO_2)_3HSO_4$ [122.7(7)−133.4(9)°].[2,3]

The molecules are involved in a strong intermolecular linkage containing I−O and I−F contacts. Each I(1) of the iodine(V) unit has five intermolecular contacts, three I−F contacts with lengths between 3.038(8) and 3.259(9) Å, one I−O contact with a length of 3.32(1) Å, and one short I−O contact of 2.77(1) Å that shows along the I(1)−O(1) bond. A distorted octahedral environment for iodine results, similar to that in IF_5.[20] The lone pair occupies one position of the octahedron and four intermolecular contacts are arranged beside it, due to the tendency of the incoming lone pairs to avoid the domains of the other electrons in the valence shell of iodine. As expected, the iodine(III) atom I(2) undergoes only one very short intermolecular I−O contact with a length of 2.50(1) Å, about 1 Å below the sum of the van der Waals radii of 3.50 Å, which results in a distorted square-planar environment around iodine.[12] The weak I(2)−O(1a) contact of 3.36(1) Å is probably caused by steric effects. All these contacts result in the formation of double layers stacked to the *a*-axis, with chlorine occupying the side positions (Figure 2). Between these layers no interactions below the sum of the van der Waals radii are found.

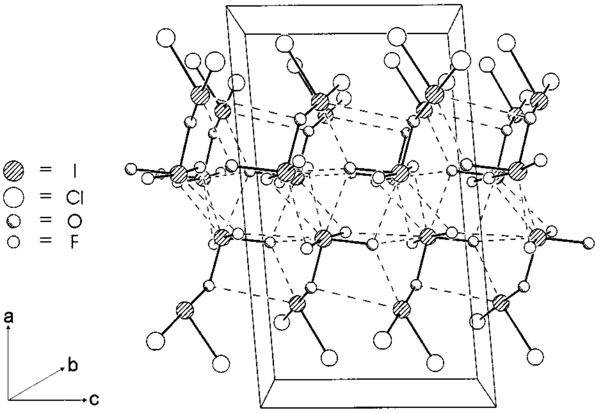

Figure 2. View of the unit cell of $Cl_2IOI(O)F_2$ in the *b*-orientation with a part of its environment; the molecules are arranged in double layers stacked on the *a*-axis and show a strong intermolecular linkage

Vibrational Spectra

The observed Raman and IR frequencies of $Cl_2IOI(O)F_2$ are summarised in Table 3 and the spectra are shown in Figure 3. The vibrational spectrum is assigned according to C_1 symmetry for $Cl_2IOI(O)F_2$, with 18 fundamental vibrations expected. The assignment has been made in comparison to known spectra of I_2Cl_6, ICl_2^+, IO_2F, IF_3O, $IO_2F_2^-$, and $(IO_2)_3HSO_4$.[21−23,3]

In the Raman spectrum, the ICl_2 stretching modes are the strongest lines and occur at 327 cm^{-1} (ν_{as} ICl_2) and 360 cm^{-1} (ν_s ICl_2). According to the relative intensities in the Raman and IR spectra, we have assigned the higher frequency to the symmetrical stretching mode. This is in agreement with the assignment for I_2Cl_6 (314 cm^{-1} ν_{as} ICl_2; 344 cm^{-1} ν_s ICl_2) and ICl_2^+ (364 cm^{-1} ν_{as} ICl_2; 371 cm^{-1} ν_s ICl_2).[21,22] The corresponding bending mode is observed at 144 cm^{-1}. The fundamental vibrations of the IF_2 group are assigned to the lines at 264 cm^{-1} (δ IF_2), 521 cm^{-1} (ν_s IF_2), and 537 cm^{-1} (ν_{as} IF_2). The stretching modes exhibit only weak intensities in the Raman spectrum, but they are observed in a typical range for axial IF_2 groups. For comparison, in KIO_2F_2 the I−F stretching modes are found at 472 and 434 cm^{-1} and in IF_3O at 515 and 550 cm^{-1}.[23] A similar behaviour is observed for the I−O stretching modes. In the Raman spectrum these have only low intensities but in the IR spectrum they are assigned to very strong bands. The stretching vibration of the I=O double bond is assigned to the bands at about 723−786 cm^{-1}, the stretching mode for the single bond I(1)−O(1) to the lines between 406 and 507 cm^{-1} and the secondary bond I(2)−O(1) to the line at 121 cm^{-1}. The complexity of the spectra in the range for the I−O stretching modes is typical for this kind of molecule and so the assignment can be made only tentatively.

Table 3. Vibrational frequencies of $Cl_2IOI(O)F_2$

Raman (T = 20 °C)	IR[a] (T = 20 °C)	Assignment
811(4)		
786(14)	776vs	ν I=O
767(9)	752vs	ν I=O
723(14)	723vs	ν I=O
	590w	
537(3)	542m	ν_{as} IF_2
521(5)	521m	ν_s IF_2
507(3)		ν I−O
	468m	ν I−O
412(4)	406m	ν I−O
389(7)	372m	δ IO_2
360(100)	354sh	ν_s ICl_2
342(17)	343m,sh	ν_s ICl_2 (I_2Cl_6)
327(67)	332/323s	ν_{as} ICl_2
	314m, sh	ν_{as} ICl_2 (I_2Cl_6)
264(7)	260vw	δ IF_2
	246vw	
228(7)	232m	δ O−I−F
218(6)	213w	δ O−I−Cl
182(3)		δ O−I−Cl
144(25)		δ ICl_2
121(25)		ν I···O
82(36)		δ I−O−I
68(44)		lattice modes
62(32)		lattice modes
52(48)		lattice modes
33(42)		lattice modes

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

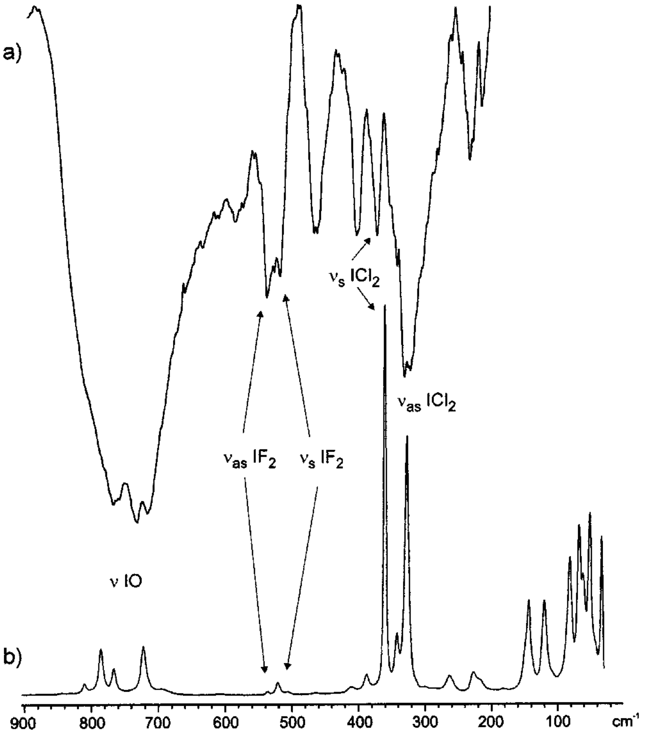

Figure 3. a) IR spectrum and b) Raman spectrum of $Cl_2IOI(O)F_2$

Experimental Section

Caution! CF_3OCl is a highly reactive oxidising agent and potentially explosive when brought into contact with organic material. Avoid contact with CF_3OCl and the other compounds described in this paper because their hydrolysis leads to the formation of HF or HCl, which cause burns and in some cases irreparable damage. Safety precautions should be taken in using and handling these materials.

All synthetic work and sample handling was performed using a standard glass vacuum line and standard Schlenk techniques. Nonvolatile materials were handled under dry nitrogen. $Cl_2IOI(O)F_2$ was obtained by the uncontrolled reaction between CF_3I, CF_3OCl, CF_2O, and Cl_2 as described above. We decided to obtain first X-ray, Raman and IR data and in the course of these studies the very small quantity of $Cl_2IOI(O)F_2$ was used up and we were not able to perform NMR spectroscopic or mass spectrometric measurements, or an elemental analysis.

The Raman spectra were recorded on a Jobin Yvon T64000 spectrometer using a Kr^+ laser (647.1 nm) from Spectra Physics. The spectra were obtained in a glass cell at room temperature.[24] Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra were obtained from a coated CsBr plate in a special IR cell.[25]

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 ω-rotation and two times 100s 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. Analysis of the duplicate reflections gave no indications of any decay.

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