Crystal Structure of (Difluoro)methoxyoxo Iodine(V) $IF_2(O)OCH_3$

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Received May 18, 2000

(Difluoro)methoxyoxo iodine(V) ($IF_2(O)OCH_3$), the methyl ester of the unknown difluoro iodic acid ($IF_2(O)OH$), was obtained by the reaction of methoxytrimethyl silane with iodine pentafluoride. $IF_2(O)OCH_3$ crystallizes orthorhombic in the space group *Pbca* with $a = 7.605(1)$ Å, $b = 7.360(1)$ Å, $c = 15.017(1)$ Å, and eight formula units per unit cell. The final R indices $[I > 2\sigma(I)]$ are R1 = 0.0264 and wR2 = 0.0516. Additionally, $IF_2(O)OCH_3$ was characterized by its vibrational spectra and quantum mechanical calculations were performed.

Introduction

The thermal stability of iodic acid is very high, and it takes temperatures of 250 °C to decompose HIO_3 into its anhydride I_2O_5.[1] For the two possible fluoro derivatives IF_4OH and $IF_2(O)OH$ no experimental evidence was reported. We think that decomposition into IF_3O or IO_2F with formation of HF is favored even at low temperatures. Since all attempts to synthesize $IF_2(O)OH$ failed, we were interested in its methyl ester $IF_2(O)OCH_3$.

In 1972 and 1974 Oates and Winfield reported metathesis reactions between IF_5 and $(CH_3)_3SiOCH_3$.[2,3] They were able to isolate new derivatives of iodine pentafluoride, described as $IF_{5-n}(OCH_3)_n$ ($n = 1-4$). The compounds were characterized by NMR and IR spectroscopy and mass spectra. In the case of IF_4OCH_3, in Pyrex at 20 °C, slow decomposition into an iodine oxofluoride with unidentified stoichiometry was observed. During our investigations concerning IF_3O and IO_2F we found a similar behavior for IF_3O.[4] The reaction between IF_5 and I_2O_5 in glass vessels at about 100 °C yielded IO_2F nearly quantitatively. When the reaction was performed in a Kel-F reactor, IF_3O was the only product as described by Aynsley et al.[5] It seems that the glass vessel reacts with formation of SiF_4 as an oxygen donator. Taking these results into consideration, it becomes reasonable that the unidentified solid observed by Oates and Winfield was probably $IF_2(O)OCH_3$. (Difluoro)methoxyoxo iodine(V) was first directly prepared in 1983 by Frohn and Pahlmann by the reaction of IF_5 with $Si(OCH_3)_4$ (eqs 1−3).[6]

$$2IF_5 + Si(OCH_3)_4 \xrightarrow{25\ °C} 2IF_3(OCH_3)_2 + SiF_4 \qquad (1)$$

$$2IF_3(OCH_3)_2 \xrightarrow{25\ °C} IF_4(OCH_3) + IF_2(OCH_3)_3 \qquad (2)$$

$$IF_2(OCH_3)_3 \xrightarrow{25\ °C} IF_2(O)OCH_3 + CH_3OCH_3 \qquad (3)$$

By variation of the molar ratio of the starting materials and the reaction conditions, the authors were able to isolate IF_4OCH_3, $IF_2(O)OCH_3$, and $IO_2(OCH_3)$.[6] The compounds were characterized by ^{19}F NMR spectroscopy. Frohn et al. found that $IF_2(O)OCH_3$ loses its solubility after crystallization, and they suggested that there are strong oxygen bridges in the solid.[6] Since no structural data for $IF_2(O)OCH_3$ or the methoxy-substituted iodine pentafluoride derivatives were reported, it was desirable to obtain single crystals of $IF_2(O)OCH_3$ to determine its crystal structure.

Experimental Section

CAUTION! *IF_5 is a highly reactive oxidizing agent. Skin contact with IF_5 and $IF_2(O)OCH_3$ should be avoided because their hydrolysis leads to HF, which causes burns and in some cases irreparable damage.*

All synthetic work and sample handling were performed using standard Schlenk techniques and a standard glass vacuum line. Nonvolatile materials were handled under dry nitrogen. Infrared spectra were recorded on a Bruker IFS 113v spectrophotometer. Spectra of dry powders were obtained in an IR cell with CsBr plates coated with the pure sample.[7] Raman spectra were recorded on a Jobin Yvon T64000 spectrometer by using a Kr^+ laser (647.1 nm, Spectra Physics). The spectra were recorded in a glass cell cooled with liquid nitrogen.[8] Single crystals were placed in Lindemann capillaries in a stream of dry nitrogen, and an X-ray diffraction study was carried out by using a Nonius Kappa CCD diffractometer.

Quantum Mechanical Calculations. Hartree−Fock calculations were performed with the program Gaussian 94.[9] For the optimization of the geometry, different starting coordinates were chosen. The calculation of the vibrational frequencies showed whether the energy-minimized structures represent stable molecules. All frequencies were positive, so that at least local minima on the Born−Oppenheimer hyperplane were found.

Preparation of $IF_2(O)OCH_3$. IF_5 (0.444 g, 2 mmol) was loaded into a dry glass vessel with greaseless stopcocks (Young). Then, 0.650 g (6 mmol) of $(CH_3)_3SiOCH_3$ was added and the mixture was held at

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10.1021/ic000525s CCC: $19.00

Table 1. X-ray Diffraction Data of $IF_2(O)OCH_3$

space group	*Pbca*
a, Å	7.605(1)
b, Å	7.360(1)
c, Å	15.017(1)
vol, Å^3	840.5(2)
$\rho_{calcd.}$, g cm^{-3}	3.349
Z	8
fw, g mol^{-1}	211.93
μ, cm^{-1}	75.30
T, °C	−100(2)
λ, Å	0.71069
R[a] [I>2σ(I)]	R1 = 0.0264, wR2 = 0.0516
R[a] (all data)	R1 = 0.0497, wR2 = 0.0569

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

room temperature for 20 min. After removal of the volatile material under vacuum at −10 °C, the formation of a yellow, viscous liquid was observed. The residue was crystallized from an SO_2 solution at −30 °C, and the crystals were finally dried in vacuo at room temperature. In most cases the yield was less than 10%. The resulting crystals were identified as $IF_2(O)OCH_3$ and stored under dry nitrogen at 25 °C.

Results and Discussion

Crystal Structure of $IF_2(O)OCH_3$. $IF_2(O)OCH_3$ crystallizes orthorhombic in the space group *Pbca* with $a = 7.605(1)$ Å, $b = 7.360(1)$ Å, $c = 15.017(1)$ Å, and eight formula units per unit cell. The crystal structure was solved by the Patterson method. A search for higher symmetry with the program X-PREP indicated no higher symmetry. A final refinement with anisotropic thermal parameters for all non-H atoms gave values of R1 = 0.0264 and wR2 = 0.0516. H atoms were taken from the difference Fourier syntheses and refined isotropically. For the data reduction, structure solution, and refinement, programs in the SHELXTL package and PARST were used.[10−12] The crystal data are summarized in Table 1.

The molecule has a pseudo trigonal bipyramidal structure with fluorine in the apical positions and nearly C_s symmetry (Figure 1). Bond lengths and angles are listed in Table 2. The I−F bonds with lengths of 1.929(3) and 1.964(3) Å are comparable to those found in IF_3O (1.91(3) and 1.89(3) Å).[13] For the I−O bonds different lengths of 1.870(3) and 1.771(3) Å are observed, indicating an I−O double bond for the latter. Oberhammer and Christe pointed out that in trigonal bipyramidal molecules double bonds can result in directional repulsive effects.[14] In $IF_2(O)OCH_3$ there are three different ligands in the equatorial plane, the methoxy group, a double-bonded oxygen, and a sterically active lone pair. The angles F(1)−I(1)−O(1) 89.3(2)° and F(2)−I(1)−O(1) 87.3(2)° between the axial fluorines and the double bond are larger than those between fluorine and the single bond. For these, values of F(1)−I(1)−O(2) 87.22(14)° and F(2)−I(1)−O(2) 86.53(14)° are found. The same effect was observed in the structure of ClF_3O by electron diffraction, and in the crystal structure of IF_3O.[13,14] To our knowledge up to now no structural data for BrF_3O were reported and so we cannot use this compound for comparison. For ClF_3O Oberhammer and Christe assumed that sterical repulsion of the π-electrons in the axial direction is larger than toward the equatorial positions.[14] The apical fluorines are bent about 4.7(2.0)° toward the space between lone pair and single bond.[14] In IF_3O the axial−equatorial angles are slightly larger than 90°, and in $IF_2(O)OCH_3$ no angle between an axial and an equatorial ligand larger than 90° is observed.[13] A population analysis for the double bond in ClF_3O showed that the electron density is distributed almost equally.[14] In these three compounds, for the equatorial plane the lone pair is the most sterically demanding ligand and the angles between the other two equatorial ligands are smaller than the ideal value of 120° (ClF_3O 108.9(0.9)°; IF_3O 99.5(1.8)°; $IF_2(O)OCH_3$ 101.4(2)°).[13,14] This comparison shows that the described effect is more pronounced for ClF_3O than for the iodine compounds where the lone pairs have the largest sterical space requirement followed by the double bonds.

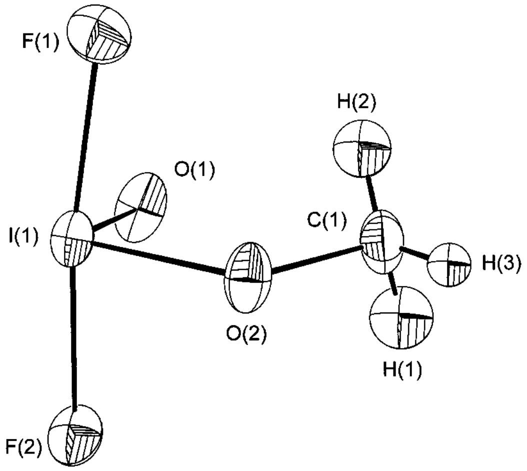

Figure 1. Projection of an $IF_2(O)OCH_3$ molecule. Thermal ellipsoids are drawn at the 50% probability level for all non-H atoms and at 25% for H atoms.

Table 2. Comparison of Calculated Bond Lengths (Å) and Selected Angles (deg) for $IF_2(O)OCH_3$ with Experimental Observed Ones

	exptl	RHF-3-21G	RHF-3-21G**
I(1)−O(1)	1.771(3)	1.8494	1.7938
I(1)−O(2)	1.870(3)	1.8959	1.8894
I(1)−F(1)	1.929(3)	1.9055	1.8950
I(1)−F(2)	1.964(3)	1.9268	1.9139
O(2)−C(1)	1.469(7)	1.4781	1.4834
C(1)−H(1)	1.04(8)	1.0740	1.0738
C(1)−H(2)	0.96(7)	1.0792	1.0777
C(1)−H(3)	0.83(6)	1.0753	1.075
O(1)−I(1)−O(2)	101.4(2)	103.1158	105.4138
O(1)−I(1)−F(1)	89.3(2)	92.7955	92.9400
O(2)−I(1)−F(1)	87.2(1)	83.5047	84.8683
O(1)−I(1)−F(2)	87.3(2)	90.3606	91.4051
O(2)−I(1)−F(2)	86.5(1)	81.7665	84.1527
F(1)−I(1)−F(2)	172.2(1)	165.2700	166.1345
C(1)−O(2)−I(1)	118.4(3)	117.6343	119.4053
O(2)−C(1)−H(1)	112(4)	109.1351	109.1350
O(2)−C(1)−H(2)	103(4)	109.7315	109.3634
O(2)−C(1)−H(3)	99(4)	104.2381	104.4129
H(1)−C(1)−H(2)	119(5)	110.5547	110.5131
H(1)−C(1)−H(3)	97(5)	111.9994	112.0964
H(2)−C(1)−H(3)	125(6)	110.9778	111.1101

Frohn et al. suggested that solid $IF_2(O)OCH_3$ is associated by oxo bridges similar to those found in I_2O_5 or IF_3O.[6,13,15] This statement can be confirmed, and additionally there are strong intermolecular iodine−fluorine interactions. As shown in Figure

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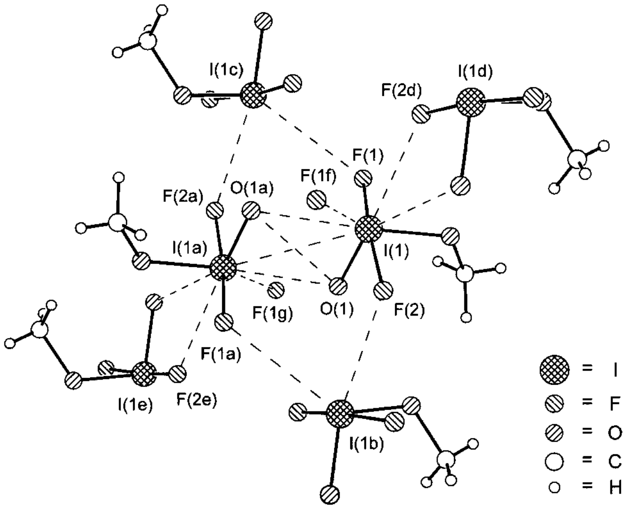

Figure 2. View of six $IF_2(O)OCH_3$ molecules with their intermolecular contacts. Each iodine has contact with three different molecules and a coordination number of 9. All these contacts result in a 3-dimensional linkage. Symmetry transformations are a = $-x, -1 - y, 2 - z$; b = $^1/_2 - x, -^1/_2 + y, z$; c = $-^1/_2 + x, ^3/_2 - y, 2 - z$; d = $^1/_2 - x, ^1/_2 + y, z$; e = $^1/_2 + x, ^1/_2 - y, 2 - z$; f = $-^1/_2 + x, ^1/_2 - y, 2 - z$; g = $-^1/_2 - x, ^1/_2 + y, z$. Thermal ellipsoids are drawn at the 50% probability level for all non-H atoms and at 25% for H atoms.

2 each iodine is an acceptor for two I−F contacts with lengths of 2.876(3) and 3.278(3) Å and two I−O contacts of 2.644(4) and 3.413(4) Å, that are shorter than the sum of the van der Waals radii published by Bondi (I−F 3.45 Å and I−O 3.50 Å).[16] When only the short interactions, I(1)−O(1a) 2.644(4) Å and I(1)−F(2d) 2.876(3) Å, are taken into consideration, a distorted octahedral arrangement for iodine results. These contacts are almost in line with the I(1)−O(2) or I(1)−O(1) bond, respectively, and can be designated as secondary bonds according to Alcock.[17] The angles formed are O(1)−I(1)−F(2d) 163.2(3)° and O(2)−I(1)−O(1a) 167.3(3)°. The intermolecular linkage results in the formation of double layers stacked along the *c*-axis. In these layers the methoxy groups occupy the terminal positions and undergo no intermolecular contacts. Between the layers no distances below the sum of the van der Waals radii are observed, indicating no significant interactions.

Vibrational Spectra. As shown by its crystal structure, isolated $IF_2(O)OCH_3$ has nearly C_s symmetry and 21 fundamentals. The assignments for $IF_2(O)OCH_3$ were made by comparison to the known literature spectra of IF_3O, IO_2F, KIO_2F_2, and those of the starting materials.[18,19] Frequencies and assignments are listed in Table 3.

Table 3. Raman and IR Frequencies of $IF_2(O)OCH_3$

Raman ($T = -196$ °C)	IR ($T = 20$ °C)[a]	assignment
3051 (10)		ν_{as} CH_3
2967 (39)	2956 vw	ν_{as} CH_3
2833 (6)	2825 vw	ν_s CH_3
	2566 br, m	
	1779 br, m	
1457 (3)	1447 w	δ_{as} CH_3
	1389 w	δ_{as} CH_3
	1203 w	δ_s CH_3
1152 (4)	1151 vw	ρ CH_3
950 (4)	978 w	ν CO
922 (10)	923 m	
826 (57)	833 m	ν I═O
	726 m	
	661 w	
617 (12)	602 m	ν_{as} IF_2
595 (100)	585 m	ν_s IF_2
517 (24)	519 s	ν I−O
470 (5)	474 s	δ C−O−I
409 (6)	398 s	δ IFO_2
357 (6)	370 s	δ IF_2O
294 (3)	288 w	δ O_c−I−F
241 (3)		δ IF_2
216 (3)		
126 (3)		lattice mode
68 (39)		lattice mode

[a] s = strong, m = medium, w = weak, vw = very weak, br = broad.

The lines at 595 and 617 cm^{-1} in the Raman spectra are assigned to ν_s IF_2 and ν_{as} IF_2, respectively. For comparison, in IF_3O the I−F stretching modes are observed at 515 and 550 cm^{-1} and in KIO_2F_2 at 472/476 and 434 cm^{-1}.[18] The corresponding IF_2 bending modes in $IF_2(O)OCH_3$ occur at 241 and 216 cm^{-1}. For the I−O double bond one line at 826 cm^{-1} and for the I−O single bond of the methoxy group one at 517 cm^{-1} are observed. Since there are two lines in the range between 922 and 978 cm^{-1}, only a tentative assignment can be made for the C−O bond. The same holds for the bending modes of the IO_2F_2 skeleton. The expected ranges and intensities are similar, and thus, the reverse assignment is also possible. The vibrations of the methyl group are expected to occur at the highest frequencies and are observed between 1151 and 3051 cm^{-1}.

Quantum Mechanical Calculations. To support the experimental results quantum mechanical calculations were carried out. $IF_2(O)OCH_3$ was calculated by ab initio (RHF-3-21G and RHF-3-21G**) methods. Table 2 shows a comparison of calculated bond lengths and angles with experimental data. Although small basis sets were used, the calculated geometries are in surprisingly good agreement with those obtained by the single-crystal X-ray structure elucidation. The I−O and I−F bond lengths are obtained in the expected areas. In particular the differences in the I−O(2) and I−O(1) bond lengths caused by their single- and double-bond characters are given quite well.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie.

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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