The structure of IF_3**

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Iodine forms four stable, binary, and neutral fluorides, IF_7, IF_5, IF_3 and IF; this is the largest number at least among nonmetal fluorides. Our knowledge of these species differs. The structure of IF_7 has been assumed pentagonal-bipyramidal for a long time but has been precisely established only recently.[1] The heptafluoride shows weak intermolecular interaction in the crystal. The most thoroughly investigated species is IF_5 and is a square pyramid with the iodine atom slightly above the basal plane defined by the four fluorine atoms.[2] A plethora of intermolecular interactions are found in the crystal, which, however, do not significantly affect the molecular structure.[3] Both compounds are thermally stable and are textbook examples of various structure–bonding models and theories.

Much less is known about IF_3 and IF. The trifluoride is the least stable binary fluoride of iodine, with a decomposition temperature of $-28\,^{\circ}C$, as established by differential thermogravimetry (IF decomposes at $-14\,^{\circ}C$).[4] This instability is in contrast also to the stability of its homologues ClF_3 and BrF_3.

If iodine is treated with diluted elemental fluorine at low temperatures, IF_3 is obtained free of IF_5.[5] The yellow solid is either insoluble in all conventional solvents, or it reacts with them. Thus information about its structure is restricted to vibrational spectroscopy.[6]

It is known that anhydrous HF dissolves traces of IF_3, as noted by a slight yellow color. Addition of small amounts of water increases the solubility and a deep brownish-yellow color results.[6] All other halogen fluorides are known to react with water under hydrolysis; this has also been described for IF_3.[6] We presume that water in small amounts acts as a base [Eq. (1)].

$$IF_3 + H_2O + HF \rightleftharpoons H_3O^+ + IF_4^- \qquad (1)$$

Enough IF_3 may go into solution to make material transport and recrystallization possible. The IF_3 is obtained in form of very thin, yellow platelets. A single crystal X-ray structure determination shows a polymeric structure (Figure 1), from which a planar T-shaped molecule can be derived on considering only the shortest I–F bonds (187.2(4), $2 \times 198.3(3)$ pm). This structure for IF_3 is expected, as is the fact that the two I–F bonds, which have a bond angle of $160.3(2)^{\circ}$ with each other, are longer than the middle I–F bond, and that all fluorine atoms of the planar molecule are positioned within one hemisphere. Remarkable are, however, the intermolecular I–F···I bridges of 276.9(3) pm. These fluorine atoms belong to the coordination sphere of two iodine atoms. It is not surprising that only the two weaker bound fluorine atoms make such bridges. Surprisingly, the resulting coordination polyhedron around the iodine atom is a planar pentagon. This is in contrast to the structure of solid BrF_3, in which the coordination of this T-shaped molecule is increased to a planar quadrilateral by one fluorine bridge.[7]

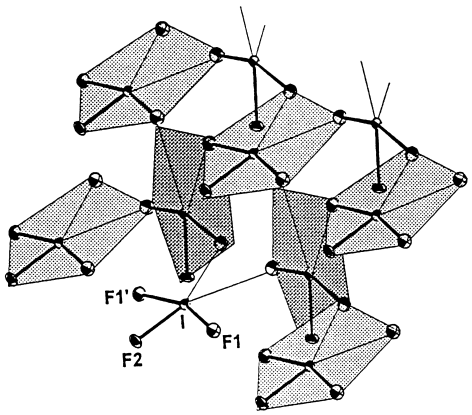

Figure 1. Section of the crystalline structure of IF_3 (ORTEP representation). Bond lengths [pm] and angles [°]: I-F1 198.3(3), I-F2 187.2(4), I···F1 276.9(3); F1-I-F2 80.2(1), F1-I-F1′ 160.3(2), F1···I···F1′ 59.5(1).

Whereas solid ClF_3 is best described as a pure molecular lattice,[8] and the structure of BrF_3 seems to contain the structure of anionic BrF_4^-, the structure of IF_3 is reminiscent of the IF_5^{2-} structure. The latter has indeed a regular planar-pentagonal structure, according to the analysis of the vibrational spectra and theoretical calculations.[9] For isoelectronic XeF_5^- this structure has been shown by crystallography.[10] A square-planar structure for IF_4^- is also known.[11]

Furthermore, IF_3 also differs from I_2Cl_6, which is known to form a double chlorine-bridged planar dimer. The transition to CF_3ICl_2, which has recently been prepared in a pure state and structurally characterized,[12] may be interesting. The CF_3ICl_2 forms planar layers with weak chlorine bridges. The resulting coordination at the iodine atom is either tetragonal planar or pentagonal planar, depending on how many chlorine contacts are taken into consideration.

A pentagonal-planar coordination as a building unit was possibly first found among Te^{IV} compounds such as $CH_3TeI[S_2CN(C_2H_5)_2]_2$.[13] These can be considered isoelectronic to IF_3 in a widest sense.

In many respects, $OTeF_5$ is the ligand most similar to a fluorine atom, if its reduced tendency to form bridged structures is overlooked.[14] For $I(OTeF_5)_3$, the T-shaped molecular structure is increased to a planar tetragon by only one, and also weaker, I···F–Te contact, just as it is found also in solid $Br(OteF_5)_3$[15] (Figure 2).

Experimental Section

IF_3: An Ar/F_2 (10/1) mixture was bubbled slowly into a suspension of I_2 in $CFCl_3$ in a poly-perfluoro-ether tetrafluoroethene (PFA) tube at $-45\,^{\circ}C$ until the I_2 disappeared completely. A yellow solid was formed in quantitative yield. Raman spectra: (cryst., $-130\,^{\circ}C$): 631 (23), 620 (73), 487 (100), 427 (14), 328 (15), 211 (45) cm^{-1}; see also ref. [6]. After the solvent had been evaporated, anhydrous HF was condensed into the tube. When the tube was opened at $-50\,^{\circ}C$, H_2O was allowed to condense into it

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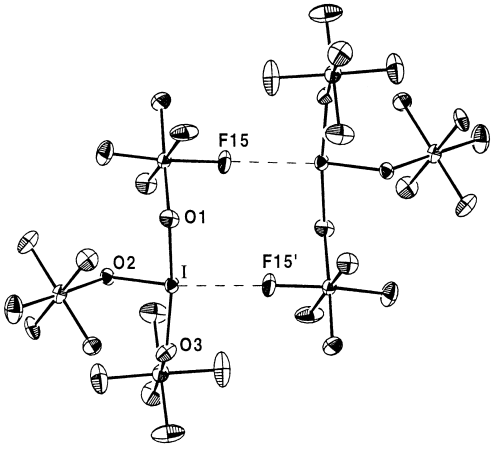

Figure 2. Crystalline structure of $I(OTeF_5)_3$ (ORTEP representation). Bond lengths [pm] and angles [°]: I-O1 208.3(5), I-O2 193.5(5), I-O3 203.3(6), I···F15 283.3(5), Te-O 183.9(5)–190.8(5), Te-F 180.8(5)–184.4(5) (F15); O1-I-O2 86.8(2), O1-I-O3 170.6(2), O2-I-O3 88.2(2) O_2-I···F15′ 171.2(2).

until the IF_3 dissolved largely or totally on shaking and the HF solution was a yellow-brown color. Warming to $-30\,^{\circ}C$ and slow cooling to $-78\,^{\circ}C$ yielded IF_3 as light-yellow platelets. With an especially designed apparatus[16] a suitable crystal was mounted on a Bruker SMART CCD 1000 TM diffractometer. Crystal structure analysis: orthorhombic, space group *Pcmn*, $a = 465.0(1)$, $b = 665.5(1)$, $c = 875.5(1)$ pm, $V = 270.9 \times 10^6$ pm^3, $T = -135\,^{\circ}C$, $Z = 4$, $Mo_{K\alpha}$ radiation, graphite monochromator, scan width of $0-3\omega$, illumination time 10 s per frame, 3279 measured, 465 independent reflections, 23 parameters, $R(F \geq 4\sigma(F)) = 0.031$, $wR_2 = 0.058$. After semi-empirical absorption correction (SADABS) the structure was solved and refined by the SHELX programs.[17]

$I(OTeF_5)_3$:[18] In a quartz vessel $CFCl_3$ (20 mL), IF_5 (1.65 g, 7.5 mmol) and $B(OTeF_5)_3$ (9.13 g, 12.5 mmol) are condensed on 635 mg (2.5 mmol) iodine at $-196\,^{\circ}C$. After the mixture had been stirred at room temperature for 2 h all volatile materials were removed under vacuum. An orange-red liquid residue slowly crystallized; the yield was almost quantitative. ^{19}F NMR (n-C_6F_{14}): Ab_4 spectrum, $\delta_A = -48.21$, $\delta_B = -45.55$, $J(AB) = 175$ Hz, $J(^{125}Te, F) = 3699$ Hz; Raman spectrum (cryst., $-150\,^{\circ}C$): 807 (20), 760 (16), 750 (8), 738 (15, sh), 730 (22), 719 (57), 713 (32, sh), 700 (62), 689 (60), 666 (97), 642 (15, sh), 635 (35), 596 (42), 492 (60), 470 (100), 449 (65), 390 (12), 346 (15), 326 (32), 314 (22, sh), 298 (25), 254 (37), 235 (59), 228 (31, sh), 215 (11), 201 (12), 177 (49), 162 (22), 130 (85), 109 (16), see also ref. [18]. Crystal structure analysis: monoclinic, space group $P2_1/c$, $a = 1447.8(1)$, $b = 973.4(1)$, $c = 1027.4(1)$ pm, $\beta = 91.42(1)$, $V = 1447.4 \times 10^6$ pm^3, $T = -128\,^{\circ}C$, $Z = 4$, 14936 measured, 1485 independent reflections, $R(F \geq 4\sigma(F)) = 0.049$, $wR_2 = 0.128$.

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, on quoting the depository numbers CSD-411036 and -411037).

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[1] K. O. Christe, E. C. Curtis, D. A. Dixon, *J. Am. Chem. Soc.* **1993**, *115*, 1520–1526; T. Vogt, A. N. Fitch, J. K. Cockcroft, *Solid State Chem.* **1993**, *103*, 275–279; R. Marx, A. R. Mahjoub, K. Seppelt, R. M. Ibberson, *J. Chem. Phys.* **1994**, *101*, 585–593.

[2] A. G. Robiette, R. H. Bradley, P. N. Brier, *J. Chem. Soc. Chem. Commun.* **1971**, 1567–1568.

[3] R. D. Burbank, G. R. Jones, *Inorg. Chem.* **1974**, *13*, 1071–1074.

[4] M. Schmeißer, P. Sartori, D. Naumann, *Chem. Ber.* **1970**, *103*, 590–593.

[5] M. Schmeißer, W. Ludovici, D. Naumann, P. Sartori, E. Scharf, *Chem. Ber.* **1968**, *101*, 4214–4220.

[6] D. Naumann, E. Renk, E. Lehmann, *J. Fluorine Chem.* **1977**, *10*, 395–403.

[7] A. M. Ellern, M. Y. Antipin, Y. T. Struchkov, V. F. Sukhoverkhov, *Zh. Neorg. Khim.* **1991**, *36*, 1393–1396; R. D. Burbank, F. N. Bensey, Jr., *J. Chem. Phys.* **1957**, *27*, 982–983.

[8] R. D. Burbank, F. N. Bensey, *J. Chem. Phys.* **1953**, *21*, 602–608.

[9] K. O. Christe, W. W. Wilson, G. W. Drake, D. A. Dixon, J. A. Boatz, R. Z. Gnann, *J. Am. Chem. Soc.* **1998**, *120*, 4711–4716.

[10] K. O. Christe, E. C. Curtis, D. A. Dixon, H. P. Mercier, J. C. P. Sanders, G. J. Schrobilgen, *J. Am. Chem. Soc.* **1991**, *113*, 3351–3361.

[11] K. O. Christe, D. Naumann, *Inorg. Chem.* **1973**, *12*, 59–62; X. Zhang, K. Seppelt, *Z. Anorg. Allg. Chem.* **1997**, *623*, 491–500.

[12] R. Minkwitz, M. Berkel, *Inorg. Chem.* **1999**, *38*, 5041–5044.

[13] D. Dakternieks, R. Di Giacomo, R. W. Gable, B. F. Hoskins, *J. Am. Chem. Soc.* **1988**, *110*, 6762–6768, see also S. Husebye, S. Esperas, *Acta Chem. Scand.* **1972**, *26*, 3293–3304.

[14] K. Seppelt, *Angew. Chem.* **1982**, *94*, 890–901, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 877–888.

[15] I. Hwang, K. Seppelt, unpublished results.

[16] H. Schumann, W. Genthe, E. Hahn, M.-B. Hossein, D. van der Helm, *J. Organomet. Chem.* **1986**, *28*, 2561–2567.

[17] G. Sheldrick, Program for Crystal Structure Solution, University of Göttingen **1986**; SHELXS-93, University of Göttingen **1993**.

[18] K. Seppelt, *Chem. Ber.* **1973**, *106*, 1920–1926.

Synthesis of the N-Terminal *N*-Myristoylated and *S*-Palmitoylated Undetrigintapeptide of Endothelial NO-Synthase**

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The correct orchestration of signal transduction from the blood stream across the endothelium to the surrounding smooth muscle cells of the blood vessels is paramount to the regulation of blood pressure. A key event in this regulation is the generation and release of NO from arginine by endothelial NO-synthase (eNOS) in response to exogeneous signals and the subsequent relaxation of the muscle cells.[1, 2] Furthermore eNOS is involved in vascular remodelling and angiogenesis,[3] and contributes to the pathogenesis of blood vessel related disorders like atheriosclerosis.[4, 5] The localization of eNOS to the plasma membrane and its concentration in the caveolae, membrane microdomains highly enriched in various signal transducing proteins is crucial to its correct biological functioning.[6]

In contrast to the other isoforms of NO-synthase identified so far, the N-terminus of eNOS is *N*-myristoylated and twice *S*-palmitoylated (see Figure 1 and **1**, Scheme 1).[7] The lipid

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