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1.1.1 Structure Investigations on Oxygen Fluorides

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1.1.3 Table of contents

The solid state structures of O_2F_2 and OF_2 resemble those in the gaseous state. Attempts to isolate the proposed $(O_2^+)_2PdF_6^{2-}$ from O_2F in HF result in the formation of $(O_2^+ H_3Pd_2F_{12}^-)_n$.

(Color image)

1.1.4 Abstract

The crystal structure of O_2F_2 is obtained at $-180^\circ C$. In the solid state the molecule has the typical hydrogen peroxide structure that has been established long ago by electron diffraction and microwave spectroscopy. OF_2 melts at $-223.8^\circ C$, so its structure is determined by powder X-ray data. The structure differs from the solid state structures of ozone and Br_2O . O_2F in its dissolved form as $O_2^+ H_nF_{n+1}^-$ oxidizes palladium to the four valence state, as found some time ago. The first product formed at low temperatures is $(O_2^+ H_3Pd_2F_{12}^-)_n$.

1.1.5 Introduction

O_2F_2 , OF_2 , and O_2F are well documented, while other compositions like O_nF_2 ($n > 2$) have never been substantiated. These three known oxygen fluorides have in common their thermodynamic instability towards decomposition into the elements, and with this their extreme oxidation/fluorination power. But their kinetic stability varies dramatically: OF_2 is stable up to $250^\circ C$, O_2F_2 at best to $-78^\circ C$. O_2F has never been isolated in a near to pure state. Usually it is observed accompanying O_2F_2 by its characteristic e.p.r. spectrum at low temperatures, or in the gas e.g. by IR spectroscopy.^{1,2} The aim of this report is to close some remaining gaps of knowledge about this class of compounds.

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1.1.6 Results and Discussion

O₂F₂

O₂F₂ is easily prepared by UV irradiation of liquid O₂/F₂ mixtures at -196° C. It shows up as brown precipitate. We prepared it so in a PFA (perfluoro-vinylether-tetrafluoro-ethene copolymerisate) capillary, pumped the excess of fluorine and oxygen off, and grew crystals directly on the x-ray diffractometer by raising and lowering the temperature around the melting point (-163° C). The crystal structure determination, as shown in figure 1 and 2, has been straight forward.

(Figure 1)

Fig. 1 O₂F₂, ORTEP representation, left: Disordered molecule. Insert: Non-disordered molecule with the two strongest residual electron densities indicating the anisotropy of the oxygen – oxygen bond.

In the gaseous state the molecule has a typical peroxide structure, with a remarkable short O-O bond length, and a fairly long O-F bond, see table 1. The question has been whether these peculiarities are retained in the solid state, and how intermolecular interactions might influence the structure. There are two O₂F₂ molecules in the asymmetric unit, one of them is disordered over two positions, so there are three molecules to consider, see figure 1. Nevertheless bond lengths and angles are the same, see table 1, except that the data of the disordered molecule are less precise. Bond angles and O-F bond lengths are the same as in the gaseous state within the errors of the measurements,³ except that the O-O bond length is shorter by 3 pm in the crystal, and with this also 3 pm shorter than in elemental oxygen! The special bond situation in the molecule can be described by the *Lewis*-structures $F-O-O-F < \text{---} > F^{\ominus} O^{\oplus}=O-F < \text{---} > F-O=O^{\oplus} F^{\ominus}$. If we use this description then the shortening of the O-bond in the solid state could be a result of intermolecular interactions between fluorine atoms and oxygen and fluorine atoms of neighboring molecules. But only one F ... F contact (267pm) and one F... O contact (280 pm) are marginally shorter than the sum of the *van der Waals* radii. In summary the intermolecular interactions are quite weak.

The crystal structure reveals a certain property of the oxygen-oxygen bond that according to the *Lewis* description as above should have multiple bond character. The two strongest residual electron densities are located next to the oxygen-oxygen bond, as shown in figure 1, indicative of a strong anisotropy of electron density of this bond. Unfortunately the data set is too limited for a complete mapping the electron density, even if only the non-disordered molecule treated as such.

It should be noted that such electron rich molecules are difficult to simulate by computational methods, even with the most sophisticated methods. For comparison the results of the possibly most advanced calculations are included in table 1.⁴

Table 1 Bond lengths (pm) and angles (°)

O₂F₂ (molecules IIa and IIb are disordered with 50% occupancy)

	O – F	O – O	F – O – O	F – O – O – F
Molecule I	161.8(2), 161.3(2)	118.6(2)	109.8(1), 110.0(1)	88.3(1)
Molecule IIa	163.7(8), 161.8(5)	118.8(6)	107.9(3), 107.9(4)	-88.4(3)

Molecule IIb	156.3(6), 163.7(4)	118.5(4)	109.7(4), 109.2(2)	86.8(5)
ED, MW ³	158.6(2)	121.6(2)	109.2(2)	88.1(4)
Calculated	153.7 ^{4a}	122.6	108.6	87.7
	170.2 ^{4b}	121.06	110.4	88.4
	161.9 ^{4c}	116.66	110.5	88.7

OF₂

OF₂ has a melting point of -223.8° C, and since our method of growing crystals had a temperature limit of about -180° C, it could not be applied here. Therefore we used a closed cycle helium cooling system method to reach the melting point temperature. All that could be done has been to get X-ray powder data. This method has been successfully applied by one of us for solving the solid state structure of ozone (mp. -192.7° C).⁵ Structurally ozone and OF₂ are related, and indeed the volume of one molecular unit OF₂ (43.5*10⁻⁶ pm³) is just a little smaller than that of O₃ (44.6*10⁻⁶ pm³). But otherwise the crystal structures are different. Solid ozone crystallizes in space group Pbca, while OF₂ at 24K crystallizes Pnam (No. 62). In one condensation and a very long measurement time at 19 K there have been indications that a partial phase change occurs possibly into space group P2₁2₁2₁ with otherwise similar lattice constants. Since this phase change is not completed the phase is not considered further.

The obtained model is shown in figure 2, numerical data are summarized in table 2. The O – F bonds come out at 140.6(12) and 142.2(12) pm and the F-O-F angle at 98.0(1.5)°. Microwave data resulted in $r_{O-F} = 140.53(4)$ and $a_{F-O-F} = 103.07(5)$ °. ⁶ The intermolecular interactions are, of course, very weak. But it is noteworthy that the shortest contacts (281 and 296 pm) are between fluorine atoms of neighboring molecules, whereas oxygen-fluorine contacts are 304 pm and larger, see figure 2. OF₂ and Br₂O have a somewhat related structure, but as expected the latter is strongly dominated by bromine – bromine contacts.⁷

(Figure 2)

Fig 2 OF₂, the unit cell viewed down the c-axis.

O₂⁺H₃Pd₄F₁₂⁻

In order to obtain O₂F in a condensed state *N. Bartlett et al.* reacted O₂⁺AsF₆⁻ or O₂⁺SbF₆⁻ with KF in anhydrous HF, so that KAsF₆ or KSbF₆ precipitate, leaving O₂F in solution of HF.⁸ These solutions are stable at -78° C and obviously contain solvated O₂F as O₂⁺ H_nF_{n+1}⁻, very much as NOF is solvated in anhydrous HF as NO⁺ H_nF_{n+1}⁻. We tried to isolate O₂F from these solutions, but again without success. These solutions are known to be extreme oxidative, oxidizing Au(III) to Au(V), Pt(IV) to Pt(V), Ag(II) to Ag(III), and Ni(II) to Ni(IV), but failed to oxidize palladium further than Pd(IV).⁸ A yellow precipitate was obtained that was described as (O₂⁺)₂PdF₆⁻².⁸ The structure of this compound would also be of interest because of the existence of two O₂⁺ cations in a small anionic environment. Under these conditions it might be possible that the two cations are forced into a four-membered ring O₄²⁺ like their heavier homologues S₄²⁺, Se₄²⁺, and Te₄²⁺. (O₂)₂ NiF₆ and (O₂)₂ MnF₆ may also be present in

similar exchange reactions in anhydrous HF.⁹ The only proven salt containing two dioxygenyl cations with a doubly charged anion is $(\text{O}_2)_2\text{Ti}_7\text{F}_{30}$, but here the two cations lie wide apart in the lattice.¹⁰

Following the published procedure indeed yellow crystals have been obtained that have been described as $(\text{O}_2)_2^+\text{PdF}_6^{2-}$, and that indeed is stable at -78°C . Our crystal structure of the same material that has never been warmed up above approximately -70°C showed that this material is $\text{O}_2^+\text{H}_3\text{PdF}_{12}^-$, with an isolated O_2^+ cation and a three dimensional, hydrogen bridged $\text{H}_3\text{Pd}_4\text{F}_{12}^-$ anion, see figure 3. Each oxygen atom is surrounded by nine F-atoms in distances of 241.8 – 308.3 pm (O1) and 242.8 – 313.1 pm (O2), much the same as in $\text{O}_2^+\text{MF}_6^-$ (M = Sb, Ru, Pt, Au).¹¹ Some of these contacts are much shorter than sum of the *van der Waals* radii of oxygen and fluorine as a consequence of the positive charge on oxygen. Also the hydrogen atoms are tightly bound, all three are bridging two fluorine atoms in the usual linear fashion creating very short F...F distances of 229.0 – 230.3 pm.

(Figure 3)

Fig 3 $\text{O}_2^+\text{H}_3\text{Pd}_4\text{F}_{12}^-$, the polymeric anion is shown as dimer through F...H...F bridging, further bridging is indicated.

1.1.7 Experimental

All manipulations were carried out under rigorously anhydrous conditions. Anhydrous HF and F_2 were handled in a stainless steel vacuum line, solids were handled in an argon filled glove box.

Single crystals were measured on a Bruker Smart CCD 1000 diffractometer with graphite monochromatized MoK_α radiation. Omega scan mode was used, and 1800 frames were measured a 20 s per frame. A semi-empirical absorption correction was applied to the data, and the structures of the single crystals were solved using the SHELXTL software.¹²

O_2F_2 : A 5mm outer diameter PFA (poly perfluoroalkoxy-vinyl tetrafluoroethene copolymerisate) tube was extended by mild heating into an approximately 0.5 mm thin capillary. This was attached to the metal vacuum line. At -196°C oxygen and fluorine (nearly 1 : 1) were condensed into it. At -196°C this mixture was irradiated by a focusable high pressure mercury lamp through a transparent glass dewar vessel. O_2F_2 is formed immediately as is indicated by a brown precipitate. After about 30 min the irradiation is stopped and the remaining gases are pumped off. The PFA capillary is sealed and mounted on the diffractometer under constant cooling. Crystal growth was done by varying the temperature around the reported melting point of -163.5°C . Formation of a single crystal was soon observed by controlling the X-ray diffraction pattern.

Crystal structure determination of O_2F_2

Crystal data. O_2F_2 , M = 70.0, monoclinic, $a = 762.6(8)$, $b = 851.8(9)$, $c = 745.7(8)$ pm, $\beta = 106.80(3)$ deg, $U = 463.7(8) \times 10^6$ pm³, $T = 153$ K, space group $\text{P2}_1/\text{c}$ (no. 14), $Z = 8$, 5212 reflections measured, 1343 unique ($R_{\text{int}} = 0.0179$), final $R(F)$ [$I > 2s(I)$] = 0.0333, final $wR(F^2)$ (all data) = 0.0732.

OF_2 : OF_2 , held in a trap at -196°C , is condensed on the copper plate at the lowest possible temperature. X-ray powder data were taken on a Huber Guinier diffractometer with Cu K_α irradiation ($\lambda = 154.18$ pm) on a copper plate cooled by a helium closed cycle cooling system. Spontaneous

crystallization starts at 20 K. The crystallization is controlled by measurement of the powder pattern. At 10 K the sharpest lines are obtained but their intensities seem to be influenced by partial ordering of the crystals. At 16 K the lines are broadened but intensities become reproducible see figure 4. The program FullProf Suite was used for solving and refining the structure¹³. The background intensity decreased and the line widths increased almost linearly from low to high 2Θ values and were fitted automatically by the program.

(Figure 4)

Fig. 4 OF_2 , experimental (x) and calculated (—) X-ray powder diagram at 16 K. Bottom: Difference curve.

60 reflections could be indexed to an orthorhombic cell with $a = 823.95(8)$, $b = 651.95(7)$, $c = 323.83(3)$ pm and $V = 173.95(3) \times 10^6 \text{ pm}^3$ and the space group Pnam (no 62, Pnma) could be established. The solution of the OF_2 structure started under the assumption, that in space group Pnam with $Z = 4$ and $c = 324$ pm the plane of the molecule should lie on the crystallographic planes at $z = 0.25$ and 0.75 . By representing the entire molecule by a single atom with very large displacement parameter the fractional coordinates x and y of the "center of gravity" of the molecule were approximated. Then the molecule with its known structure in the gas phase has been put in there, and the proper orientation was found by trial and error. Finally the molecular structure was refined with $R(F) = 0.139$.

Table 2 OF_2 : Atomic coordinates and equivalent isotropic displacement parameters U_{eq} (10 nm^2)

	x	y	z	U_{eq}
F1	.1094(6)	-.1614(6)	.2500	0.035(2)
F2	.1994(5)	.0316(6)	.2500	0.035(2)
O1	.3559(5)	-.0554(7)	.2500	0.035(2)

$(\text{O}_2^+ \text{H}_3 \text{Pd}_2 \text{F}_{12})_n$: The preparation follows the published procedure for the attempted preparation of $(\text{O}_2)_2 \text{PdF}_6$, $\text{O}_2 \text{AsF}_6$ and $\text{K}_2 \text{PdF}_6$ in a molar ratio 2 : 1 are reacted at -78°C in anhydrous HF. The yellow solution is decanted from a nearly colorless precipitate. At -78°C excess HF is pumped off. At no time the temperature is allowed to raise above -78°C . When the volume of the solution is reduced to about 20% yellow crystals begin to form. These are isolated on a special device that allows immediate mounting of one crystal on the diffractometer.

Crystal structure determination of $(\text{O}_2^+ \text{H}_3 \text{Pd}_2 \text{F}_{12})_n$

Crystal data. $\text{F}_{12}\text{H}_3\text{O}_2\text{Pd}_2$, $M = 475.8$, triclinic, $a = 558.5(3)$, $b = 974.4(7)$, $c = 978.4(6)$ pm, $\alpha = 112.28(5)$, $\beta = 100.09(5)$, $\gamma = 102.60(5)^\circ$, $U = 460.8(5) \times 10^6 \text{ pm}^3$, $T = 133 \text{ K}$, space group P-1 (no. 2), $Z = 2$, 3774 reflections measured, 2557 unique ($R_{\text{int}} = 0.0109$), final $R(F)[I > 2s(I)] = 0.0220$, final $wR(F^2)$ (all data) = 0.0540.

Full structural data are included in the Electronic Supplementary Information and have been submitted to the CCDC 1406168 (O_2F_2) and 1406169 ($\text{H}_3\text{F}_{12} \text{O}_2\text{Pd}_2$). These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Further details of the powder crystal structure

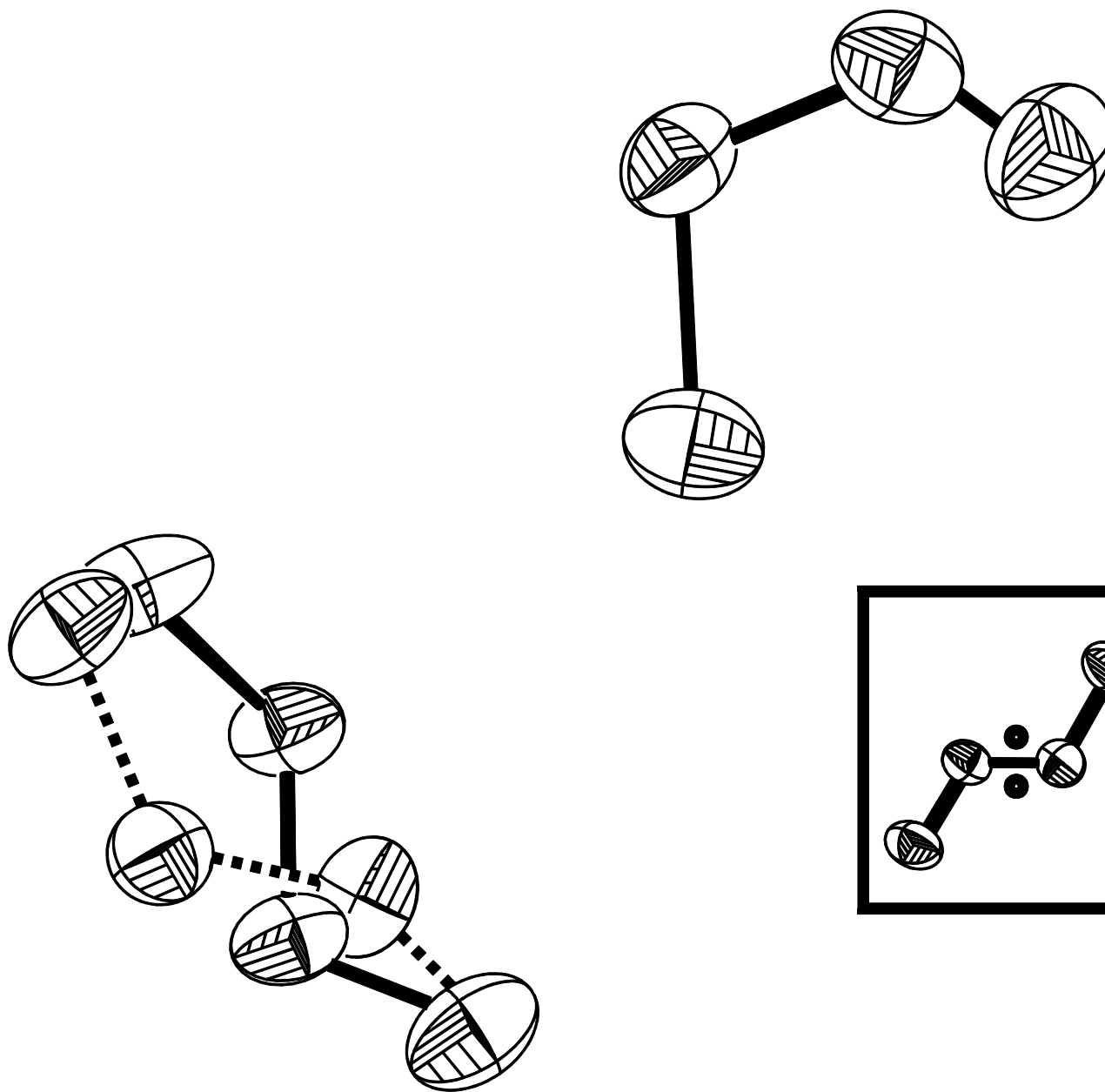
determination of OF₂ may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD xxxxx.

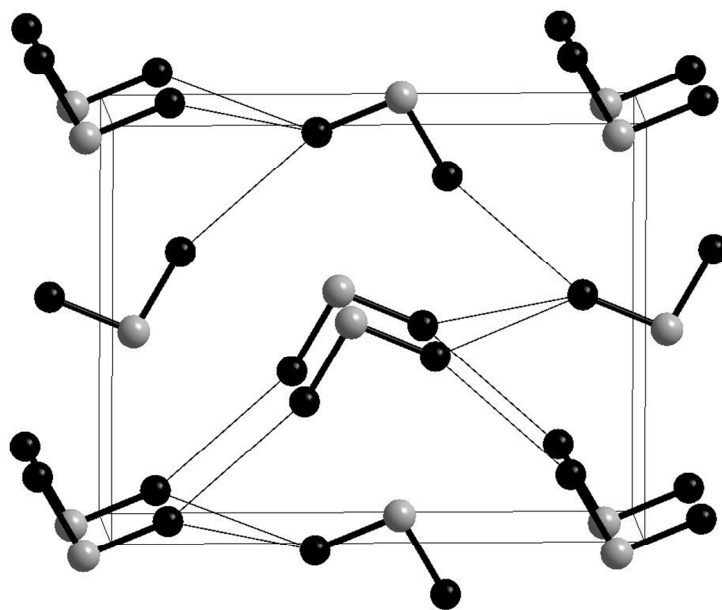
1.1.8 Conclusion

This work closes some gaps in the knowledge about oxygen fluorides. We have found no indication about the existence of any other oxygen fluoride, especially not during the photolytic preparation of O₂F₂.

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