Crystal structure of bis(fluorosulfato-κO)xenon(II), Xe(SO$_3$F)$_2$

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Thermally unstable Xe(SO$_3$F)$_2$ has been prepared by the reaction of XeF$_2$ with HSO$_3$F. Single crystals were obtained from HSO$_3$F by slow cooling in a sealed tube. The molecular structure is characterized by the Xe atom covalently bonded to two O atoms of two fluorosulfate tetrahedra in an almost linear fashion [O—Xe—O = 179.13 (4)°]. The crystal packing is strongly influenced by intermolecular van der Waals forces.

1. Chemical context

In 1972, Neil Bartlett published data on the unit cell of Xe(SO$_3$F)$_2$ (Wechsberg *et al.*, 1972). As a result of the thermal instability of this compound, no further structural details were given at that time, but ^{19}F and ^{129}Xe NMR spectra were reported subsequently (Gillespie *et al.*, 1974; Schrobilgen *et al.*, 1978). The decomposition of Xe(SO$_3$F)$_2$ leads cleanly to Xe and S$_2$O$_6$F$_2$.

2. Structural commentary

Analogous to XeF$_2$ (Agron *et al.*, 1963), the two-coordinated xenon atom adopts a linear geometry [angle O1—Xe—O4 = 179.13 (4)°]. The molecule has nearly C_i symmetry, with the xenon atom at the pseudo-inversion centre (Fig. 1). This finding is in contrast to earlier reports, where C_s symmetry was discussed based on Raman spectroscopic data (Gillespie & Landa, 1973). The Xe—O bonds are 2.1101 (13) and 2.1225 (13) Å, which is typical for Xe—O single bonds, whereas Xe=O double bonds are considerably shorter with lengths $\simeq$ 1.75 Å. The related compound xenon fluoride fluorosulfate, XeF(OSO$_2$F) (Bartlett *et al.*, 1969, 1972),

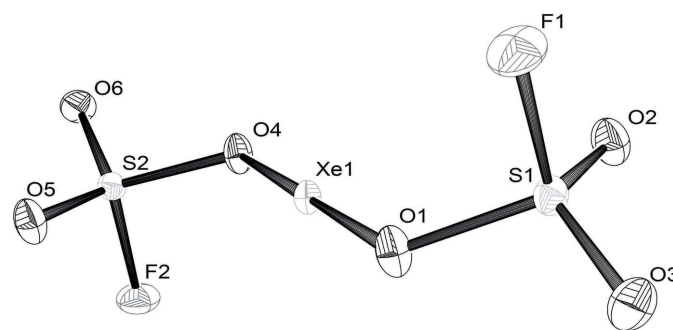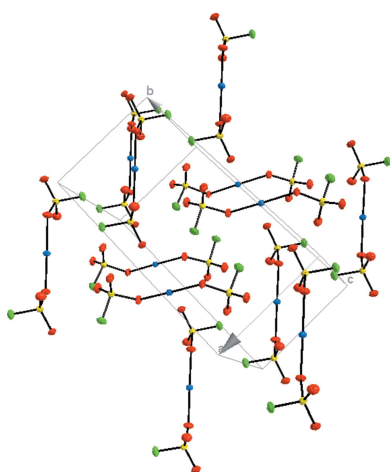**Figure 1**
The molecular structure of the title compound, with displacement ellipsoids drawn at the 50% probability level.
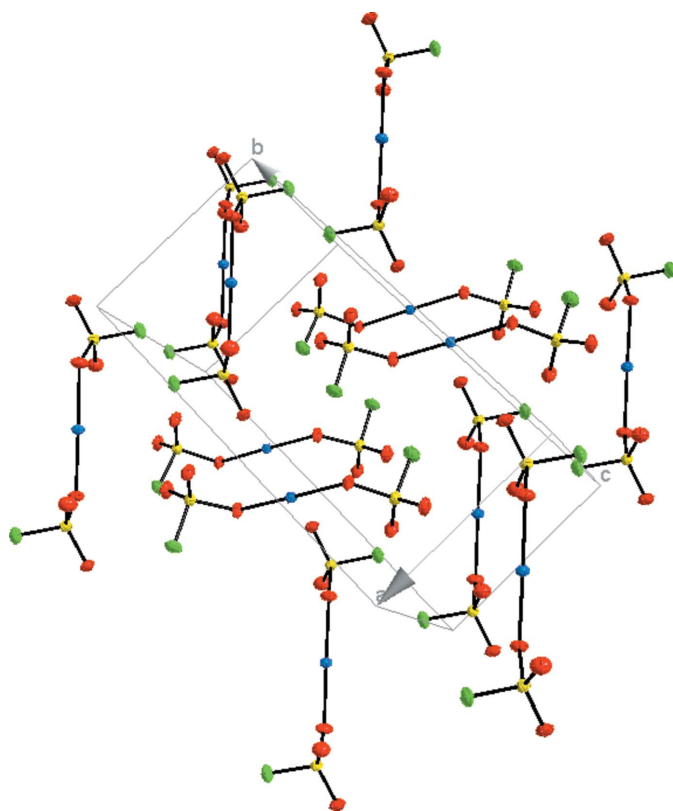
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Figure 2
The crystal packing of the title compound

Table 1
Selected geometric parameters (Å, °).

Xe1—O1	2.1101 (13)	S1—F1	1.5449 (12)
Xe1—O4	2.1225 (13)	S2—O6	1.4141 (13)
S1—O3	1.4103 (13)	S2—O5	1.4150 (14)
S1—O2	1.4092 (14)	S2—O4	1.5237 (13)
S1—O1	1.5334 (13)	S2—F2	1.5483 (12)
O1—Xe1—O4	179.13 (4)		

Table 2
Intermolecular contacts (Å).

Xe1···O2	3.1613 (15)	Xe1···F1^{iv}	3.4551 (17)
Xe1···O5	3.1855 (16)	Xe1···O3^{v}	3.4707 (19)
Xe1···O2^{i}	3.1872 (17)	Xe1···O5^{vi}	3.4818 (18)
Xe1···O6^{ii}	3.2317 (19)	Xe1···F2^{vii}	3.5867 (17)
Xe1···O6^{iii}	3.3262 (18)		

Symmetry codes: (i) $-x, -y+1, -z+2$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x+1, y, z$; (v) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (vii) $x-1, y, z$.

seconds to remove HF, then frozen with liquid nitrogen and sealed. The yellow product ($\simeq$ 0.2 ml) was warmed to 273 K and the PFA tube placed in a dewar filled with 273 K ethanol and cooled slowly to 193 K in a freezer. The light-yellow single crystals of $Xe(SO_3F)_2$ that had formed were decanted off and mounted in a cold nitrogen stream. At 100 K, the crystals are colorless. The compound decomposes rapidly in moist air and can ignite organic materials.

contains a Xe—O bond that is slightly longer [2.155 (8) Å] than in the title compound, but the Xe—F bond of XeF(OSO$_2$F) is at 1.940 (8) Å shorter than that in XeF$_2$ (2.00 Å). For XeF(OSO$_2$F), partial ionic bonding (XeF$^+$·OSO$_2$F$^-$) was discussed. Obviously, both XeF$_2$ and Xe(SO$_3$F)$_2$ have a higher covalent character. The S—O bonds in Xe(SO$_3$F)$_2$ involving the O atoms that are also bonded to the xenon atom (S1—O1 and S2—O4) are about 0.1 Å longer than the terminal S—O bonds (Table 1), indicating partial double-bond character.

3. Supramolecular features

The crystal packing (Fig. 2) is strongly influenced by intermolecular van der Waals interactions to seven oxygen atoms and two fluorine atoms (Table 2). Whereas the xenon atom in XeF$_2$ exhibits intermolecular interactions to eight fluorine atoms (distance 3.42 Å; Agron *et al.*, 1963), XeF(OSO$_2$F) has fewer contacts (five contacts to oxygen in the range 3.28–3.49 Å and one contact to fluorine of 3.39 Å; Bartlett *et al.*, 1972).

4. Synthesis and crystallization

550 mg fluorosulfuric acid were placed in a 8 mm PFA tube. 170 mg (1 mmol) of XeF$_2$ were added and the mixture vigorously shaken at room temperature for some minutes until all XeF$_2$ had dissolved. The PFA tube was evacuated for some

Table 3
Experimental details.

Crystal data	
Chemical formula	[Xe(SO$_3$F)$_2$]
M_r	329.42
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	6.706 (3), 13.237 (6), 7.769 (3)
β (°)	96.50 (3)
V (Å^3)	685.2 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	5.66
Crystal size (mm)	0.50 × 0.40 × 0.15
Data collection	
Diffractometer	Bruker CCD SMART 2000
Absorption correction	Multi-scan (*SADABS*; Bruker, 2006)
T_{min}, T_{max}	0.545, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11036, 2096, 1978
R_{int}	0.020
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.033, 1.11
No. of reflections	2096
No. of parameters	101
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.69

Computer programs: *SMART* and *SAINT* (Bruker, 2006), *SHELXS97*, *SHELXL* and *SHELXTL* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999).

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3.

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Crystal structure of bis(fluorosulfato-*κO*)xenon(II), Xe(SO₃F)₂

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Computing details

Data collection: *SMART* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT* (Bruker, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Bis(fluorosulfato-*κO*)xenon(II)

Crystal data

[Xe(SO₃F)₂]	$F(000) = 608$
$M_r = 329.42$	$D_x = 3.194$ Mg m⁻³
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 999 reflections
$a = 6.706$ (3) Å	$\theta = 2.0–21.0°$
$b = 13.237$ (6) Å	$\mu = 5.66$ mm⁻¹
$c = 7.769$ (3) Å	$T = 100$ K
$\beta = 96.50$ (3)°	Irregular, colorless
$V = 685.2$ (5) Å³	$0.50 \times 0.40 \times 0.15$ mm
$Z = 4$	

Data collection

Bruker CCD SMART 2000 diffractometer	11036 measured reflections
Radiation source: fine-focus sealed tube	2096 independent reflections
Graphite monochromator	1978 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.020$
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	$\theta_{max} = 30.6°$, $\theta_{min} = 3.1°$
	$h = -9 \rightarrow 8$
	$k = -18 \rightarrow 18$
$T_{min} = 0.545$, $T_{max} = 1.000$	$l = -11 \rightarrow 9$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.013$	$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 0.4262P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.033$	
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.002$
2096 reflections	$\Delta\rho_{max} = 0.56$ e Å⁻³
101 parameters	$\Delta\rho_{min} = -0.69$ e Å⁻³
0 restraints	Extinction correction: SHELXL (Sheldrick, 2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0244 (5)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Xe1	0.000928 (13)	0.627394 (6)	0.726096 (13)	0.01145 (4)
S1	−0.33404 (6)	0.46260 (3)	0.75371 (5)	0.01295 (8)
S2	0.32649 (6)	0.79932 (3)	0.70775 (5)	0.01265 (8)
O4	0.24243 (18)	0.72199 (8)	0.82568 (16)	0.0155 (2)
F2	0.51324 (16)	0.74159 (8)	0.65972 (16)	0.0227 (2)
O2	−0.22016 (19)	0.45699 (9)	0.91739 (17)	0.0190 (2)
F1	−0.52083 (16)	0.52658 (9)	0.78020 (16)	0.0255 (2)
O6	0.4027 (2)	0.88225 (8)	0.80947 (18)	0.0181 (2)
O5	0.2017 (2)	0.81316 (9)	0.55006 (17)	0.0202 (3)
O3	−0.4069 (2)	0.37545 (9)	0.6629 (2)	0.0218 (3)
O1	−0.23650 (18)	0.53141 (9)	0.62828 (16)	0.0168 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Xe1	0.01151 (6)	0.01094 (6)	0.01174 (7)	−0.00098 (3)	0.00068 (3)	0.00171 (3)
S1	0.01200 (16)	0.01179 (15)	0.0150 (2)	−0.00106 (12)	0.00137 (13)	0.00063 (13)
S2	0.01379 (17)	0.01185 (15)	0.01261 (19)	−0.00147 (12)	0.00274 (13)	−0.00024 (13)
O4	0.0159 (5)	0.0156 (5)	0.0143 (6)	−0.0052 (4)	−0.0010 (4)	0.0026 (4)
F2	0.0194 (5)	0.0234 (5)	0.0268 (6)	0.0023 (4)	0.0093 (4)	−0.0049 (4)
O2	0.0216 (6)	0.0210 (5)	0.0141 (6)	−0.0027 (5)	0.0004 (5)	0.0033 (5)
F1	0.0158 (5)	0.0232 (5)	0.0382 (7)	0.0055 (4)	0.0064 (5)	−0.0005 (5)
O6	0.0221 (6)	0.0147 (5)	0.0181 (7)	−0.0052 (4)	0.0047 (5)	−0.0038 (4)
O5	0.0240 (6)	0.0219 (6)	0.0141 (6)	−0.0038 (5)	−0.0006 (5)	0.0044 (5)
O3	0.0243 (6)	0.0164 (6)	0.0248 (8)	−0.0070 (4)	0.0026 (5)	−0.0041 (5)
O1	0.0167 (5)	0.0191 (5)	0.0139 (6)	−0.0064 (4)	−0.0022 (4)	0.0033 (4)

Geometric parameters (Å, º)

Xe1—O1	2.1101 (13)	S1—F1	1.5449 (12)
Xe1—O4	2.1225 (13)	S2—O6	1.4141 (13)
S1—O3	1.4103 (13)	S2—O5	1.4150 (14)
S1—O2	1.4092 (14)	S2—O4	1.5237 (13)
S1—O1	1.5334 (13)	S2—F2	1.5483 (12)
Xe1···O2	3.1613 (15)	Xe1···F1iv	3.4551 (17)

Xe1···O5	3.1855 (16)	Xe1···O3[v]	3.4707 (19)
Xe1···O2[i]	3.1872 (17)	Xe1···O5[vi]	3.4818 (18)
Xe1···O6[ii]	3.2317 (19)	Xe1···F2[vii]	3.5867 (17)
Xe1···O6[iii]	3.3262 (18)		
O1—Xe1—O4	179.13 (4)	O6—S2—O4	108.69 (8)
O3—S1—O2	122.00 (8)	O5—S2—O4	112.64 (8)
O3—S1—O1	108.46 (8)	O6—S2—F2	105.47 (8)
O2—S1—O1	112.23 (7)	O5—S2—F2	105.68 (8)
O3—S1—F1	105.94 (8)	O4—S2—F2	100.24 (7)
O2—S1—F1	105.86 (8)	S2—O4—Xe1	119.74 (7)
O1—S1—F1	99.77 (7)	S1—O1—Xe1	119.18 (7)
O6—S2—O5	121.62 (8)		

Symmetry codes: (i) −x, −y+1, −z+2; (ii) x−1/2, −y+3/2, z−1/2; (iii) −x+1/2, y−1/2, −z+3/2; (iv) x+1, y, z; (v) −x−1/2, y+1/2, −z+3/2; (vi) x−1/2, −y+3/2, z+1/2; (vii) x−1, y, z.