

[Ni₂Nb₂Te₄] and [Ni₂Ta₂Te₄] (Huang, Liu & Huang, 1991).

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Structure of Disulfuryl Difluoride at 100 K

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Abstract. S₂O₅F₂, *M_r* = 182.07, tetragonal, *P*4̄2₁*c*, *a* = 7.5214 (5), *c* = 9.2610 (10) Å, *V* = 523.9 Å³, *Z* = 4, *D_x* = 2.308 Mg m⁻³, λ(Mo Kα) = 0.71073 Å, μ = 0.975 mm⁻¹, *F*(000) = 360, *T* = 100 K, *R* = 0.024 for 433 unique observed reflections. Molecules of S₂O₅F₂ occupy special positions on twofold axes. Principal bond lengths and angles are: S—O 1.6108 (11); S=O 1.3947 (20), 1.4021 (18); S—F 1.5215 (16) Å; S—O—S 123.44 (7); O—S=O 109.82 (8), 104.46 (9); O—S—F 98.34 (7); O=S—F 107.42 (9), 108.16 (10); O=S=O 125.35 (11)°. The molecule adopts a different conformation in the crystal from that previously observed in the gas phase.

Introduction. Disulfuryl difluoride was first prepared by the reaction of SbF₅ with SO₃ (Hayek & Koller,

1951). It is a liquid at room temperature (m.p. 225 K, b.p. 324 K) and is sensitive to moisture. Although the structure of the free molecule is known from gas-phase electron diffraction (Hencher & Bauer, 1973), its solid-state structure was unknown. We undertook the determination of the crystal structure in part to allow comparison between the molecule in the two phases.

Experimental. The title compound was prepared by the reaction of SbF₅ with SO₃ (Hayek & Koller, 1951). The crude product was purified by repeated distillation and its purity checked by Raman spectroscopy (Toužín & Černík, 1992). A sample of the liquid was sealed in a Pyrex capillary tube and slow cooling on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) yielded a single crystal which was held at 100.0 (1) K for the duration of the

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experiment. Lattice parameters were refined using the 2θ values of 57 reflections ($30 < 2\theta < 32^\circ$) measured at $\pm\omega$. Intensities were measured by ω - 2θ scans with the ω -scan width given by $(0.99 + 0.347\tan\theta)^\circ$ to $2\theta_{\max} = 60^\circ$. No significant variation in the intensities of 3 standard reflections was observed. The structure was solved by automatic direct methods (*SHELXS86*; Sheldrick, 1986) and refined by full-matrix least squares on F (*SHELX76*; Sheldrick, 1976), observed reflections only, with weights $w^{-1} = [\sigma^2(F) + 0.00056(F)^2]$. Other programs used were: *CALC* (Gould & Taylor, 1985) for molecular geometry calculations, and *PLUTO* (Motherwell & Clegg, 1978) and *ORTEPII*, interactive version (Mallinson & Muir, 1985) for the preparations of the illustrations. Experimental data are summarized in Table 1.*

Discussion. Fractional atomic coordinates appear in Table 2 and derived molecular parameters in Table 3. A view of a single molecule showing the atom-numbering scheme adopted appears as Fig. 1, while Fig. 2 shows the molecular packing. The structure of disulfuryl difluoride is composed of isolated molecules with only weak intermolecular interactions. These molecules are formed by two $[\text{SO}_2\text{F}]$ tetrahedra sharing a common O atom. Each S atom has contacts to two O atoms, one from the other tetrahedron in the same molecule and one from a neighbouring molecule [at $(1 + y, 1 - x, -z)$] at distances of 3.094 (2) and 3.134 (2) Å, respectively, slightly less than the sum of the van der Waals radii for S and O (1.85 + 1.40 Å; Pauling, 1952). The molecules possess crystallographic twofold symmetry and the $[\text{SO}_2\text{F}]$ groups are staggered by $144.97(5)^\circ$ about the $\text{S}\cdots\text{S}$ vector, in contrast to the structure of the molecule as determined by gas-phase electron diffraction (GPED) (Hencher & Bauer, 1973) where a structure without a twofold axis is favoured and the $[\text{SO}_2\text{F}]$ groups are staggered by $119.1(6)^\circ$. Average terminal $\text{S}-\text{O}$ [1.398 (3) Å] and $\text{S}-\text{F}$ [1.5215 (16) Å] bond lengths compare closely with those found in other sulfuryl halides: 1.402 (3) and 1.525 (12) in $\text{S}_3\text{O}_8\text{F}_2$ (GPED), 1.386 (2) and 1.514 (2) in SO_2F_2 (solid state), 1.408 (3) and 1.538 (1) in SO_2ClF (solid state) (Mootz & Merschenz-Quack, 1988) and 1.403 (3) and 1.552 (4) (equatorial), 1.575 (4) Å (axial) in SOF_4 (GPED) (Gunderson & Hedberg, 1969). The $\text{S}-\text{O}$ bridging distances in $\text{S}_2\text{O}_5\text{F}_2$ and $\text{S}_3\text{O}_8\text{F}_2$ are rather short, presumably less than the single-bond distance. The shortening is ascribed to delocalization

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55452 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0109]

Table 1. *Experimental details*

Crystal dimensions (cylinder)	0.4 × 0.4 × 1.0 mm
Range of h, k, l	0 to 10, 0 to 7, 0 to 12
Standard reflections	513, 350, 226
Number of reflections measured	512
Number of unique reflections	452
R_{int}	0.007
Number of observed reflections [$F > 4\sigma(F)$]	433
Parameters refined	43
Secondary-extinction parameter	$2.6(3) \times 10^{-6}$
R	0.024
wR	0.035
S	1.182
$(\Delta/\sigma)_{\text{max}}$ in final cycle	0.003
$(\Delta\rho)_{\text{min}}, (\Delta\rho)_{\text{max}}$ ($e \text{ \AA}^{-3}$)	-0.3, 0.4

Table 2. *Atomic coordinates and thermal parameters (\AA^2) with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
S	0.67174 (6)	0.07795 (7)	0.13701 (5)	0.0176 (3)
O(1)	0.5	0.0	0.21942 (19)	0.0209 (9)
O(2)	0.70643 (22)	-0.02340 (24)	0.01310 (18)	0.0238 (8)
O(3)	0.79347 (23)	0.1132 (3)	0.24695 (21)	0.0361 (10)
F	0.59251 (20)	0.25385 (18)	0.08757 (17)	0.0273 (7)

Table 3. *Interatomic distances (\AA), valence and torsion angles ($^\circ$) in crystalline $\text{S}_2\text{O}_5\text{F}_2$ and equivalent distances found in the gas phase by electron diffraction*

	Crystal	Gas*
$\text{S}-\text{O}(1)$	1.6108 (11)	1.611 (5)
$\text{S}-\text{O}(2)$	1.4021 (18)	1.398 (2)
$\text{S}-\text{O}(3)$	1.3947 (20)	
$\text{S}-\text{F}$	1.5215 (16)	1.525 (5)
$\text{S}-\text{O}(1)-\text{S}^i$	123.44 (7)	123.6 (5)
$\text{O}(1)-\text{S}-\text{O}(2)$	109.82 (8)	106.1 (9)
$\text{O}(1)-\text{S}-\text{O}(3)$	104.46 (9)	
$\text{O}(1)-\text{S}-\text{F}$	98.34 (7)	102.4 (18)
$\text{O}(2)-\text{S}-\text{F}$	107.42 (9)	106.6 (6)
$\text{O}(3)-\text{S}-\text{F}$	108.16 (10)	
$\text{O}(2)-\text{S}-\text{O}(3)$	125.35 (11)	126.8 (12)
$\text{F}-\text{S}\cdots\text{S}^i-\text{F}^i$	144.97 (5)	119.1 (6)

Symmetry code: (i) $1 - x, -y, z$.

* Hencher & Bauer (1973).

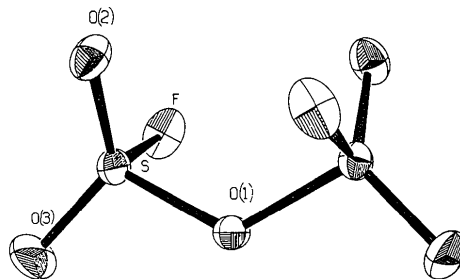


Fig. 1. A view of a single molecule of disulfuryl difluoride. The two asymmetric units shown are related by a twofold axis passing through O(1). Thermal ellipsoids are drawn at the 30% probability level.

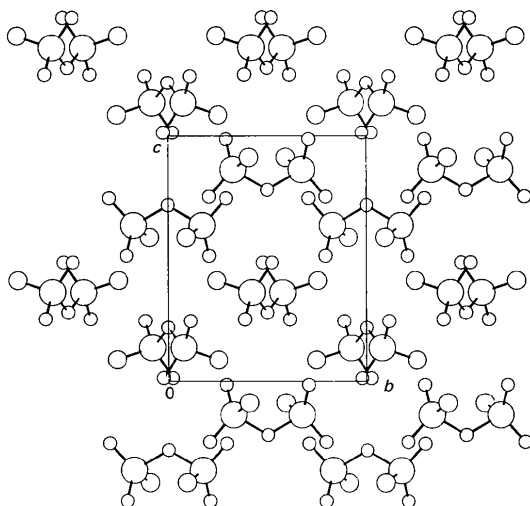


Fig. 2. A packing diagram showing the arrangement of molecules as viewed along the *a* axis.

and back donation of free-electron pairs on the O atom to an S atom polarized by its halogen substituents (Hencher & Bauer, 1973). This effect is even more pronounced in F_5SOSF_5 (solid state) (Oberhammer & Seppelt, 1978), where a short S—O bridging distance [1.586 (11) Å] is compensated for by increased S—F bond lengths [1.560 (4) Å] and the large S—O—S angle of 142.5 (16)° can be attributed to both steric hindrance and a significant π contribution to the S—O—S bonds compared with tetrahedrally coordinated polysulfuryl halides.

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Low-Temperature Commensurate Phase of Potassium Tetrachlorozincate, K_2ZnCl_4

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Abstract. K_2ZnCl_4 , $M_r = 285.4$, monoclinic, Cc , $a = 14.394$ (7), $b = 24.544$ (8), $c = 26.616$ (5) Å, $\beta = 89.98$ (3)°, $V = 9405.0$ (56) Å³, $Z = 48$, $D_x = 2.42$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 5.546$ mm⁻¹, $F(000) = 6528$, $T = 140$ K, final $R = 0.043$ for 7124 independent reflections with $F > 5\sigma(F)$. The structure is modified a little from the room-temperature commensurate phase of $P2_1cn$ ($Z = 12$). The $ZnCl_4$ tetrahedra that have rather large thermal parameters at room temperature deviate especially from the $P2_1cn$ structure by shifts along

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the *a* axis and rotation about axes parallel to the *c* axis.

Introduction. K_2ZnCl_4 is a ferroelectric compound that performs the normal-incommensurate and the incommensurate-commensurate transitions (Gesi, 1978; Gesi & Iizumi, 1979), as does K_2SeO_4 (Iizumi, Axe, Shirane & Shimaoka, 1977). The crystal structures of the normal phase above 553 K and the incommensurate phase between 403 and 553 K have been analyzed by Quilichini, Bernede, Lefebvre &