

The Isomers of S_2F_2

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THE preparation of a pure sample of one isomer of S_2F_2 , its vapour pressure, b.p., infrared spectrum, and some other properties were described by Seel and Göllitz.¹ Subsequently a second

isomer was reported^{2,3} but not thoroughly characterized. On the basis of infrared and mass-spectral evidence it was inferred⁴ that the first isomer was thiothionyl fluoride (SSF_2 ; b.p. -10.6°) and that

¹ F. Seel and D. Göllitz, *Chimia (Switz.)*, 1963, **17**, 207; *Z. anorg. Chem.*, 1964, **327**, 32.

² F. Seel and R. Budenz, *Chimia (Switz.)*, 1963, **17**, 335.

³ F. Seel, R. Budenz, and D. Werner, *Chem. Ber.*, 1964, **97**, 1369.

⁴ F. Seel and R. Budenz, *Chem. Ber.*, 1965, **98**, 251.

the second was difluorodisulphane (FSSF). Independently, two isomeric S_2F_2 species were characterized in terms of detailed geometries by their microwave spectra^{5,6} taken on a mixture containing both isomers. However no correspondence with the pure isomers in bulk was established.

We have prepared pure samples of both isomers using the reaction of silver fluoride and sulphur and conclusively identified them by their microwave spectra.

Our specimen of SSF_2 had vapour pressures, b.p., and infrared spectrum⁷ in full agreement with those reported by Seel and his co-workers. Excellent agreement with previously reported microwave lines of SSF_2 and lines calculated from its rotation constants was found (see Table).

Similar satisfactory agreement with reported and calculated microwave lines of FSSF (see Table) has been obtained for the other isomer. It gave satisfactory analyses and molecular weight and its infrared spectrum was identical with that previously reported.⁴ The m.p. was -133° . The vapour pressure of FSSF was measured between -65° and 30° in a Monel and Kel-F system. At higher temperatures the isomerization to the more stable SSF_2 proceeded rapidly enough to preclude accurate measurements. The measured pressures are reproduced by the equation $\log p$ (mm.) = $7.44 - 1310/T$, the extrapolated normal boiling point being $+15^\circ$. These results contrast with previous reports on this isomer^{2,3}

in which it was described as more volatile than SSF_2 , although no vapour pressure data were given. Contrary to reports by Seel and Budenz⁴ we have not experienced particular difficulty in separating a mixture of the isomers by trap-to-trap distillation, SSF_2 being the more volatile constituent in such manipulation. In the light of this the evidence for the existence of a molecular complex of the two isomers⁴ seems unconvincing.

Microwave spectral identification of SSF_2 and FSSF

Transition	Measurements		
	present	previous ⁶	Calc.*
	SSF_2		
$0_{00}-1_{10}$	12147.38	12147.40	12147.27
$3_{12}-3_{23}$	11324.48	11324.42	11324.85
$1_{10}-2_{11}$	14937.43	14937.61	14937.61
$4_{13}-4_{23}$	9666.33		9666.78
	FSSF		
$0_{00}-1_{11}$	13843.62	13843.37	13843.37
$1_{01}-1_{10}$	8703.88		8703.33
$2_{02}-2_{11}$	8919.90		8919.15
$3_{03}-3_{12}$	9250.80		9250.19
$4_{04}-4_{13}$	9706.28		9705.10
$5_{05}-5_{14}$	10296.45		10295.16
$6_{06}-6_{15}$	11035.80		11033.88
$2_{21}-3_{12}$	9101.55		9103.09

* From previously published rotation constants,⁶ rigid rotor approximation.

(Received, May 31st, 1965.)

⁵ R. L. Kuczkowski and E. B. Wilson, *J. Amer. Chem. Soc.*, 1963, **85**, 2028.

⁶ R. L. Kuczkowski, *J. Amer. Chem. Soc.*, 1963, **85**, 3047; 1964, **86**, 3617.

⁷ R. D. Brown, G. P. Pez, and M. F. O'Dwyer, *Austral. J. Chem.*, 1965, **18**, 627.