

In contrast, it was found that "3-isoadenosine" is unable to replace adenosine in supporting the growth of mammalian cells cultures²⁴ in a system requiring an exogenous purine source²⁵ for optimal growth.

Forthcoming reports from our Laboratory will discuss the work in detail, the phosphorylation of 3- β -D-ribofuranosyladenine or "3-isoadenosine," and its conversion to other derivatives isomeric with those of adenosine.

(24) Human HeLa and murine NCTC-1742 cell strains. I. S. Johnson, *Ann. N. Y. Acad. Sci.*, **76**, 543 (Dec. 5, 1958); I. S. Johnson, J. Vlantis, B. Mattas and H. F. Wright, Canadian Cancer Conference, Academic Press, New York and London, Vol. 4, 344 (1961).

(25) M. T. Hakala and E. Taylor, *J. Biol. Chem.*, **234**, 126 (1959).

(26) U. S. Public Health Service Predoctoral Fellow, 1962-1964.

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Microwave and Mass Spectra of Sulfur Monofluoride¹

Sir:

The preparation of S₂F₂ has been claimed by a number of investigators.²⁻⁵ More recently an infrared spectrum was assigned to this species.⁶ However, doubts have been expressed about the characterization^{7,8} and existence of S₂F₂.⁹ Using methods similar to those of the earlier workers, we have prepared S₂F₂ and have positively identified it as S₂F₂ by means of its mass and microwave spectra. We further determined the structure which turns out to be an analog of the well known SOF₂.

Approximately 1 g. of argentous fluoride (AgF) and 6 g. of sulfur were mixed and slowly heated *in vacuo* in glass to the melting point of sulfur. The gases produced were condensed with liquid N₂. Microwave absorption lines were observed due to SO₂ and SOF₂ as well as additional lines. The mass spectrum indicated SiF₄, SO₂ and SOF₂ as well as peaks at 83 and 102 *m/e* units. The analysis of the mass spectrum, taking into account the presence of SiF₄, SO₂ and SOF₂ and the expected isotopic contributions from sulfur, led to the tentative conclusion that the new microwave lines were due to S₂F₂.

Drying of AgF *in vacuo* reduced the SO₂, SiF₄ and SOF₂ content and increased the S₂F₂ yield. It also brought in microwave and mass peaks due to SF₄. Low temperature fractional distillation produced a sample which we estimate contained approximately 90% S₂F₂ with SO₂, SOF₂ and SF₄ as impurities. The relative mass spectral cracking pattern obtained after correction for SO₂, SOF₂ and SF₄ is reported in Table I.

The microwave spectrum of S₂F₂ was observed and assigned to transitions, largely with the aid of the Stark patterns and the fit to a rigid rotor formula (see Table II). In addition to the spectrum of the main species, weaker satellite lines were found which had approximately the correct relative intensity to be sulfur-34

(1) This work was made possible by support extended Harvard University by the Office of Naval Research.

(2) M. Centnerswer and C. Strenk, *Ber.*, **56**, 2249 (1923); **58**, 914 (1925).

(3) O. Ruff, *Angew. Chem.*, **46**, 739 (1933).

(4) M. Trautz and K. Ehrmann, *J. Prakt. Chem.*, **142**, 79 (1935).

(5) L. M. Dubnikov and N. Zorin, *J. Gen. Chem. USSR*, **17**, 185 (1947).

(6) B. Matutana and C. Otero, *Anales real. soc. espan. fis. quim.* (Madrid), **51B**, 223 (1955); **53B**, 195 (1957).

(7) G. Cady, "Advances in Inorganic Chemistry and Radiochemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1962.

(8) I. W. George, "Progress in Inorganic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960.

(9) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 417.

TABLE I

RELATIVE MASS SPECTRAL CRACKING PATTERN FOR S₂F₂^a

Mass/charge	Relative abundance	Assignment
102	100	S ₂ F ₂ ⁺
83	30.2	S ₂ F ⁺
70	7.4	SF ₂ ⁺
64	23.2	S ₂ ⁺
51	6.6	SF ⁺ (S ₂ F ₂ ⁺⁺)
32	26.6	S ⁺ (S ₂ ⁺⁺)
19	2.6	F ⁺
41.5	~0.6	S ₂ F ⁺⁺
35	<0.1	SF ₂ ⁺⁺

^a Obtained with Consolidated Engineering Corporation spectrometer Model 21-103c at 70 ionizing volts and 10- μ a. ionizing current.

lines and the correct temperature dependence of intensity (also see Table II). Table III shows the rotational constants and moments of inertia extracted from the analyzed spectra. These were used to determine the structure of S₂F₂, applying several alternative standard methods. The bond distances and angles shown in Fig. 1 carry limits of error which generously cover the variations among these methods.

TABLE II

MICROWAVE SPECTRUM OF S₂F₂^a

Transition	Observed	Calculated
S ³² S ³² F ₂		
0 ₀₀ → 1 ₁₀	12147.40	12147.27
1 ₀₁ → 2 ₁₁	20083.62	20083.57
1 ₁₀ → 2 ₁₁	14937.61	(14937.61) ^b
1 ₁₁ → 2 ₁₂	13067.63	(13067.63)
2 ₁₂ → 2 ₂₀	15577.32	15576.99
1 ₁₁ → 2 ₂₁	28505.50	(28505.50)
2 ₁₁ → 3 ₂₁	34312.85	34313.12
3 ₂₂ → 3 ₃₀	23486.60	23486.75
4 ₂₃ → 4 ₃₁	23915.70	23916.24
S ³² S ³⁴ F ₂		
0 ₀₀ → 1 ₁₀	12068.54	(12068.54)
1 ₀₁ → 2 ₁₁	19969.03	(19969.03)
1 ₁₁ → 2 ₂₁	28304.60	28305.14
2 ₁₂ → 3 ₂₂	36205.45	36205.62
2 ₁₁ → 3 ₂₁	34109.39	34108.86
3 ₂₂ → 3 ₃₀	23230.90	(23230.90)
S ³⁴ S ³² F ₂		
0 ₀₀ → 1 ₁₀	12007.65	(12007.65)
1 ₀₁ → 2 ₁₁	19676.66	(19676.66)
1 ₁₁ → 2 ₂₁	28353.30	28353.95
3 ₂₂ → 3 ₃₀	23972.04	(23972.03)
4 ₂₃ → 4 ₃₁	24341.36	24340.95

^a Obtained with a conventional Stark modulated spectrometer. Frequencies reproducible to ± 0.1 Mc. ^b Transitions in parenthesis used to calculate rotational constants.

This structure is very similar to that of SOF₂ in which¹⁰ the sulfur-fluorine distance is 1.58 Å., angle FSF is 92.8° and angle FSO is 106.8°. The sulfur-sulfur distance in S₂ is reported¹¹ to be 1.89 Å.

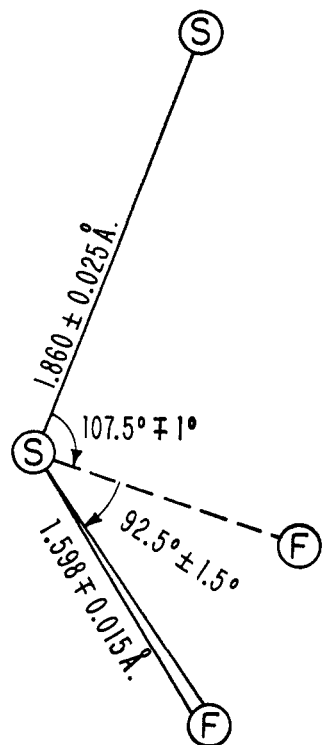
The basis for asserting that the above microwave spectrum is due to S₂F₂ is as follows. (1) The intensity of these microwave lines obtained from different samples with different purification steps correlate with mass spectral analysis indicating the amount of S₂F₂. (2) The structure obtained by assuming that the empirical composition is S₂F₂ is almost identical with that predicted from the known structure of SOF₂.

(10) R. C. Ferguson, *J. Am. Chem. Soc.*, **76**, 850 (1954).

(11) L. E. Sutton, Ed., "Tables of Interatomic Distances," Special Publication No. 11, Chem. Soc. London, 1958.

TABLE III
 ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR S₂F₂

	S ³² S ³² F ₂	S ³² S ³⁴ F ₂	S ³⁴ S ³² F ₂
A	8179.12 ± 0.1 Mc.	8118.30 ± 0.2 Mc.	8173.15 ± 0.2 Mc.
B	3968.15 ± .1 Mc.	3950.24 ± .1 Mc.	3834.50 ± .1 Mc.
C	3033.16 ± .1 Mc.	3030.90 ± .4 Mc.	2955.48 ± .4 Mc.
I _A	61.8075 ± 0.0010 Amu. Å. ²	62.2705 ± 0.0016 Amu. Å. ²	61.8527 ± 0.0016 Amu. Å. ²
I _B	127.3971 ± .0030	127.9748 ± .0030	131.8375 ± .0030
I _C	166.6681 ± .0055	166.7989 ± .0300	171.0556 ± .0300
I _A + I _C - I _B	101.0785 ± .0095	101.0946 ± .0346	101.0708 ± .0346

Fig. 1.—Structure of S₂F₂.

(3) The microwave data alone and the moments of inertia obtained therefrom are only reasonable for S₂F₂, for from these data one can show that the molecule contains at least two non-equivalent atoms of sulfur, that it does not contain any other elements which have two or more isotopic species in appreciable abundance, that it is non-planar and therefore has more than three atoms, that the two sulfur atoms lie in a plane of symmetry so that there is at least one equivalent pair of other atoms out of this plane, and finally that the molecule is almost certainly S₂F₂ because other choices lead to interatomic parameters which would conflict either with known ranges of non-bonded distances or known ranges of bonded distances.

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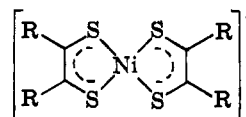
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RECEIVED MAY 27, 1963

E.s.r. Studies of Four-Coördinate Complexes of Nickel, Palladium and Platinum Related by Electron Transfer Reactions

Sir:

The peculiar diamagnetic nickel complex 1 (R = C₆H₅, z = 0) reported by Schrauzer and Mayweg,¹ and considered by them to be planar, bears a definite rela-

(1) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

M = Ni, Pd, Pt

tion to the anionic complexes of bivalent metals²⁻⁴ with the dimercaptomaleonitrile anion, (NC)₂C₂S₂⁻².^{2,5} Specifically, the diamagnetic nickel complex 2 (R = CN, z = -2) has two more electrons associated with the metal and the chelate rings than does 1. Herein we report a novel series of electron transfer reactions, effected both chemically and electrochemically, whereby we have obtained certain of the corresponding members (same z-values) of three series of complexes with R = C₆H₅, CN, CF₃.

Treatment of 1 in dimethylsulfoxide (DMSO) solution with *p*-phenylenediamine produces the anion 3 (R = C₆H₅, z = -1), which gives a strong electron spin resonance signal in DMSO solution with $\langle g \rangle = 2.0568 \pm 0.0003$. The anion can be isolated as the paramagnetic (C₆H₅)₄As⁺ (1.86 B.M.) and Et₄N⁺ (1.82 B.M.) salts.⁶ The latter salt in DMSO solution has $\mu_{\text{eff}} = 1.80$ B.M. The reduction reaction is readily reversed by I₂ in CH₂Cl₂ solution. Enrichment of 3 in Ni⁶¹ (I = 3/2) indicates the odd electron is localized at least partially on the metal by virtue of the observable electron-nucleus hyperfine splitting, $|a| = 4.5 \pm 1$ gauss. Reaction of 2 or of the corresponding palladium (4) and platinum (5) complexes (R = CN, z = -2) with I₂ in DMSO solution followed by rapid dilution with an ethanolic solution of tetraethylammonium bromide produced the nickel (6) or the palladium (7) and platinum (8) complexes as black crystalline air-stable 1:1 salts. The moment of solid 6 was found to be ~ 1.0 B.M. at room temperature, indicating significant exchange demagnetization; however, in acetone solution $\mu_{\text{eff}} = 1.83$ B.M., in reasonable agreement with the observed $\langle g \rangle = 2.0633 \pm 0.0004$. This compound represents the first recognized example of a four-coördinate complex containing nickel in a doublet state.⁷ Complex 7 is a diamagnetic solid and 8 is a weakly paramagnetic solid (~ 1.1 B.M.) at room temperature. In 50% v./v. chloroform-dimethylformamide solutions these complexes give intense e.s.r. signals with $\langle g \rangle = 2.0238 \pm 0.0002$ (7) and 2.042 ± 0.001 (8).⁸ In both complexes the hyperfine splitting from the naturally occurring magnetic metal isotopes

(2) G. Bähr and G. Schleitzer, *Ber.*, **90**, 438 (1957).(3) H. B. Gray, R. Williams, I. Bernal and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).(4) E. Billig, R. Williams, I. Bernal and H. B. Gray, *Inorg. Chem.*, in press.(5) H. E. Simmons, D. C. Blomstron and R. D. Vest, *J. Am. Chem. Soc.*, **84**, 4756 (1962).

(6) All compounds referred to herein gave highly satisfactory analyses for carbon and hydrogen and, where appropriate, nitrogen, sulfur and fluorine.

(7) Another example may be the complex formulated as K₂Ni(CN)₄ and reported to have a moment of 1.73 B.M.: cf. R. Nast and T. von Krakay, *Z. Naturforsch.*, **9b**, 798 (1954).

(8) Relatively low solubility and slow reaction have thus far prevented accurate measure of magnetic susceptibilities in solution.