[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE, THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, AND THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

A Verification of the Molecular Structure of Pentafluorosulfur Hypofluorite (SF_5OF) by Electron Diffraction[1,2]

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The structure of pentafluorosulfur hypofluorite (SF_5OF) has been investigated by electron diffraction from the gas. The results support the proposed hypofluorite structure and indicate that the molecule has octahedrally coördinated sulfur with the O–F bond in staggered configuration. The average S–F distance is 1.53 Å. and the O–F and S–O distances appear to be about 1.43 and 1.64 Å., in the normal range. The best agreement was obtained from models with oxygen bond angles near the tetrahedral value, F–S–F bond angles very close to 90°, and the opposed S–F and S–O bonds non-colinear by a few degrees.

Dudley, Cady and Eggers have prepared an interesting compound with the formula SOF_6 by the reaction of fluorine and thionyl fluoride at 200° in the presence of silver difluoride.[3] The properties of SOF_6 are suggestive of a hypofluorite, and the presence of an O–F group in the molecule was verified by the infrared[3] spectrum and by the nuclear paramagnetic resonance spectrum.[4] It seemed worthwhile to carry out an electron-diffraction investigation, too, from which one could hope to learn more details of the structure even though its over-all complexity would prevent a precise evaluation of many of the interesting parameters.

Experimental

The sample of SF_5OF was prepared in the way described,[3] refined to a high state of purity and maintained in a bomb fitted with a needle valve which had been previously deactivated by repeated contact with the substance. Electron-diffraction photographs were prepared in the new California Institute of Technology apparatus using a rotating sector with angular opening proportional to s^3; the camera distance was 9.63 cm. and the electron wave length (obtained in a separate experiment on solid zinc oxide) was 0.0620 Å. Four carefully selected plates were microphotometered while being rotated rapidly about the axis of the diffraction rings in order to minimize the effect of emulsion grain, and the traces reduced in essentially the way described by Bastiansen, Hedberg and Hedberg.[5] The experimental intensity curve, obtained after computing a radial distribution curve from a preliminary experimental curve and redrawing the experimental background in the usual way so as to eliminate the obvious errors, is shown in Fig. 1.[6]

Analysis and Results

The radial distribution curve (shown in Fig. 2) was calculated[5] using an Alwac III-E digital computer from the equation

$$rD(r) = \sum_s I(s) \exp(-1.2 \times 10^{-3} s^2) \sin rs$$

taking $I(s)$ at intervals $\Delta s = 0.5$ over the range $0.5 \leqslant s \leqslant 45$. It shows two major peaks, at 1.53 and 2.18 A., which are, respectively, due to bonded interactions and to non-bonded interactions through one bond angle; the ratio of these distance values (1.42) is about $2^{1/2}$, corresponding to an average bond angle of about 90° and substantiating the notion of octahedral bonding at the sulfur atom. The general correctness of the octahedral structure is further proved by the good fits to all the minor peaks of the radial distribution curve given by models of this geometry having reasonable S–O and S–F distances and reasonable S–O–F bond angles.

A determination of each of the many structural parameters for SF_5OF by refining a suitable trial structure seemed not to be worthwhile to us because although such might be possible by use of the least squares procedure,[5] the data seemed insufficient to give usefully small standard errors.[7] The analysis was restricted, therefore, to a trial and error procedure aimed at finding reasonable models giving as good fits as possible to the data. The search for models was confined to models of C_s symmetry with a staggered configuration of the O–F bond (Fig. 3), as seemed to be indicated by the radial distribution curve. The parameter ranges investigated[8] were

$$1.525 \text{ Å.} \leqslant \text{S–F}_1 = \text{S–F}_2 = \text{S–F}_4 = \text{S–F}_5 \leqslant 1.540 \text{ Å.}, 1.510 \text{ Å.} \leqslant \text{S–F}_3 \leqslant 1.580 \text{ Å.}, 1.530 \text{ Å.} \leqslant \text{S–O} \leqslant 1.650 \text{ Å.}, 1.420 \text{ Å.} \leqslant \text{O–F}_6 \leqslant 1.500 \text{ Å.}, 2° \leqslant \phi \leqslant 10°, 107° \leqslant \theta \leqslant 112°, 90° \leqslant \text{F}_3\text{–S-plane of F}_4\text{F}_5\text{S} \leqslant 94°, \text{and } 88° \leqslant \text{F}_3\text{–S-plane of F}_1\text{F}_2\text{S} \leqslant 90°$$

No attempt was made to investigate the vibration factors. Theoretical radial distribution curves were calculated for about twenty models by summing Gauss curves of areas equal to the weights of the terms ($nZ_iZ_jr_{ij}^{-1}$) positioned on a distance scale such that the maxima corresponded to interatomic distances in the model; the half-widths of the peaks (which are related to the vibrational displacements of the pair of atoms) were given reasonable values and varied somewhat when necessary to get better agreement. For several of these models theoretical

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[1] Published as Research Paper 358 from Oregon State College and Contribution No. 2440 from Gates and Crellin Laboratories, California Institute of Technology.

[2] This work is taken from the Ph.D. thesis of Roger A. Crawford, Department of Chemistry, Oregon State College, 1958.

[3] F. B. Dudley, G. H. Cady and D. F. Eggers, Jr., THIS JOURNAL, **78**, 1553 (1956).

[4] F. B. Dudley, J. N. Shoolery and G. H. Cady, *ibid.*, **78**, 568 (1956).

[5] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

[6] The undiffracted electron beam was caught in a stop which obstructed the pattern for $s < 4$. The experimental intensity curve for $0 < s < 4$ was obtained visually from non-sector photographs made without a beam stop; interpretations and measurements of one of the authors (K.H.) and Dr. Verner Schomaker were used.

[7] For example, the S–O, the O–F and the three types of S–F distances demanded by the symmetry of the simplest geometry lie unresolved under the 1.53 Å. peak. There are thus large correlations among the various distances and the associated vibration factors.

[8] The assumptions invoked in order to reduce the structural parameters to a manageable number undoubtedly do not conform to the real structure. Nonetheless, the good fit to the data eventually obtained with such models suggests either that the real structure is not far removed from these models or that the various parameters are correlated in such a way as to be adequately represented by many sets of values.

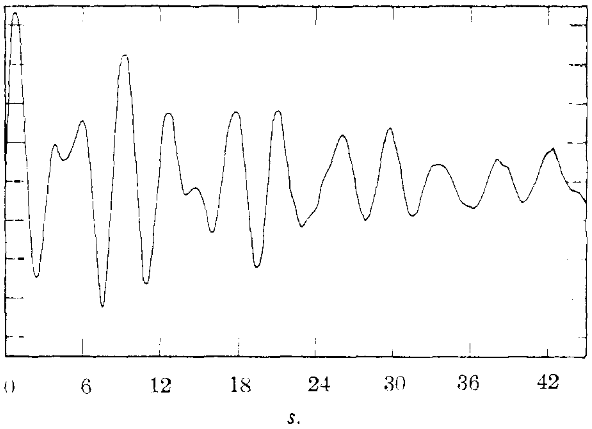

Fig. 1.—Experimental intensity curve for SF_5OF. The portion of the curve $0 < s < 2$ is from a theoretical intensity curve, the portion $2 < s < 4$ from visual observation and the rest from microphotometer traces.

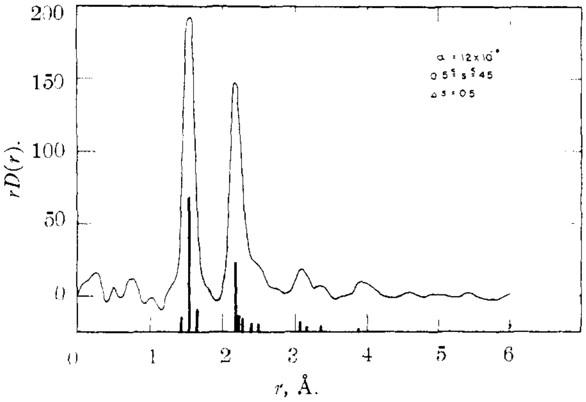

Fig. 2.—Radial distribution curve for SF_5OF. The exponential convergence factor coefficient, range of data and data interval used are given at upper right. The vertical bars correspond to the interatomic distances for the model giving the intensity curve shown in Fig. 4.

intensity curves were calculated[5] using the Alwac III-E computer according to the equation

$$I(s) = \sum_{i,j} Z_i Z_j r_{ij}^{-1} \exp(-a_{ij}s^2) \sin r_{ij}s$$

An example of a curve corresponding to one of the best models is shown in Fig. 4; the corresponding structural parameters are given in the legend.

In all models giving good agreement with the data the average S–F bond distance was about 1.53 Å., in agreement with values found in other compounds. Although little can be said about the relatively weakly scattering O–F and S–O distances (they are not resolved from the S–F distances in the 1.53 Å. peak), they appear to be of normal length. The S–O–F_6 bond angle in the better models is also about normal, being somewhat greater than the 103.2° found for F_2O[9] and somewhat less than the values found when the two peripheral groups are large. An F_3–S–O angle slightly different from 180° and the O–F bond in staggered configuration seemed to be necessary for good agreement and may be attributed to steric effects. The over-all structure of the SF_6O– grouping in SF_5OF seems to be the same, within experimental error, as that found in SF_5OOSF_5.[10]

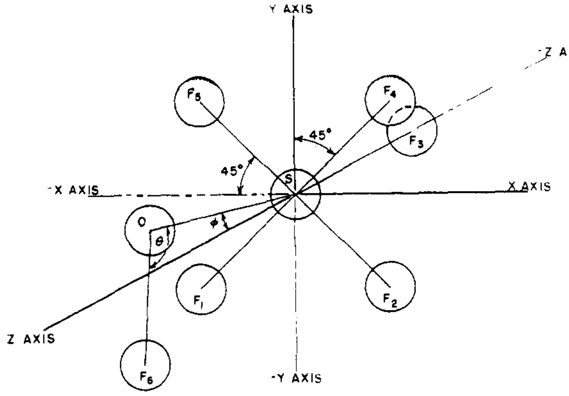

Fig. 3.—Diagram of the SF_5OF molecule.

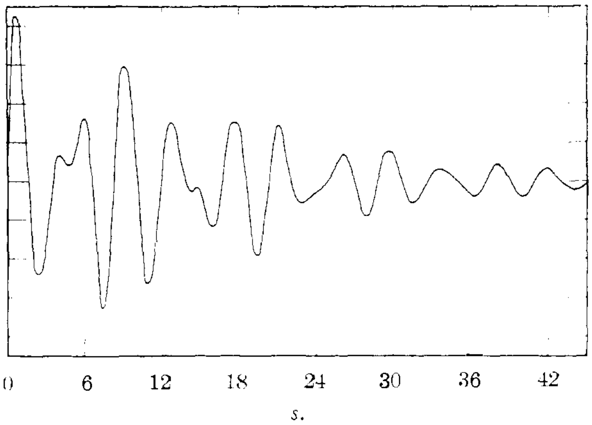

Fig. 4.—Theoretical intensity curve for an acceptable model of SF_5OF. The parameter values are $S–F_1 = S–F_2 = S–F_4 = S–F_5 = 1.530$ Å., $S–F_3 = 1.530$ Å., $S–O = 1.640$ Å., $O–F_6 = 1.430$ Å., $\phi = 2°$, $\theta = 108°$, $\angle F_3$–S-plane of $F_4F_5S = \angle F_3$–S-plane of $F_1F_2S = 90°$.

In summary, our results support completely the proposed hypofluorite structure, and while they do not permit detailed conclusions about many of the interesting structural parameters, they do suggest reasonable values for the more important ones.

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[9] J. A. Ibers and V. Schomaker, *J. Phys. Chem.*, **57**, 699 (1953.)

[10] R. B. Harvey and S. H. Bauer, THIS JOURNAL, **76**, 859 (1954).