arise from hydrolysis of the trimethylsulfonium methyl sulfate, was observed.

The initial crystalline material was isolated by the following procedure. To trimethylmethylthiosilane (6.3 g., 52.5 mmoles) in a Schlenk tube was added dimethyl sulfate (13.2 g., 105 mmoles). After the first signs of precipitation were observed, the reaction mixture was cooled to 0° and left overnight. The crystalline precipitate was filtered off, and the filtrate was transferred to a two-neck flask and returned to a cold bath. The colorless crystals were washed with two 20-ml. portions of benzene and dried under vacuum (1.5 g.). The infrared spectrum was identical with that of authentic trimethylsulfonium methyl sulfate.

After 1 week at 0° the mother liquors had deposited a further quantity (1.7 g.) of trimethylsulfonium methyl sulfate and two liquid layers had formed. The upper was characterized as hexamethyldisiloxane and the lower consisted essentially of dimethyl sulfate. A strong odor of sulfur dioxide was also detected during the work-up procedure.

(b) **Trimethylmethylthiogermane.**—To trimethylmethylthiogermane (9.1 g., 55.1 mmoles) in a two-neck flask was added dimethyl sulfate (14.0 g., 111 mmoles) at room temperature, and then the reaction mixture was cooled to 0°. After 3 days the total reaction mixture was transferred, as an ether slurry, to a Schlenk tube, and the white crystalline material was removed by filtration (9.7 g.; 93% yield). The infrared spectrum was identical with that of authentic trimethylsulfonium methyl sulfate. The ether solution was fractionated to give trimethylgermylmethyl sulfate (b.p. 55–57° (0.2 mm.); 70% yield). The p.m.r. spectrum showed two peaks, −77.5 c.p.s. (CH_3Ge–) and −259.6 c.p.s. (CH_3O–), relative to an external tetramethylsilane standard. The integrated areas were in the ratio 3:1. Bands characteristic of $(CH_3)_3Ge$– were observed in the infrared spectrum at 635 (ν_{as} Ge–C_3), 785 (CH_3–Ge rock), and 1250 cm.$^{-1}$ (symmetric deformation of CH_3– (Ge)). A strong band was also observed at 970 cm.$^{-1}$ which could be due to a stretching mode of vibration of the Ge–O–S system.

Anal. Calcd. for $C_4H_{12}GeSO_4$: C, 21.0; H, 5.3. Found: C, 21.3; H, 5.3.

(8) **Reaction with Silver(I) Iodide.**—To silver(I) iodide (5.5 g., 23.5 mmoles) in a small distilling apparatus was added bis-(trimethylsilyl) telluride (2.3 g., 9.1 mmoles). Immediate reaction was indicated by the silver(I) iodide turning black. The temperature of the reaction mixture was raised slowly to 120° and the trimethyliodosilane distilled off (99%). Characterization was by infrared and p.m.r. spectroscopy (CH_3–Si protons at −47.3 c.p.s. from internal tetramethylsilane). The presence of iodine in the distillate was confirmed qualitatively.

Preparation of Sodium Triphenylgermanethiolate.[6]—Triphenylbromogermane (7.2 g., 18.8 mmoles) in benzene (60 ml.) was added dropwise to a suspension of *anhydrous* sodium sulfide (7.2 g., 93 mmoles) in dry ethanol (110 ml.). After 30 min. the reaction mixture was filtered under nitrogen and the clear filtrate evaporated under vacuum to give a white residue. This residue was extracted with benzene in a Schlenk tube and the benzene filtrate evaporated to dryness. The residue contained no sodium and was extracted with hexane to give ethoxytriphenylgermane (2.5 g., 38% yield, m.p. 86–87°). The infrared spectrum showed bands at 911 and 1060 cm.$^{-1}$ due to the Ge–O–C system.

Anal. Calcd. for $C_{20}H_{20}GeO$: C, 68.8; H, 5.8. Found: C, 69.2; H, 5.5.

The hexane-insoluble material gave hexaphenyldigermoxane (2.5 g., 43% yield, m.p. 183–184°). The infrared spectrum showed absorption at 861 cm.$^{-1}$ due to the Ge–O–Ge group.

The procedure was repeated except for the use of sodium sulfide·$x$hydrate purified by recrystallization from an aqueous solution (1.5 *M*) of sodium hydroxide, two recrystallizations from anhydrous ethanol, and then drying for 3 hr. at 65° and 10^{-2} mm. pressure. The white crystalline product, sodium triphenylgermanethiolate, melted in the range of 180–197°, was water soluble, and decomposed as previously described.[6]

Acknowledgments.—This research was supported by the Alfred P. Sloan Foundation and by the Advanced Research Projects Agency of the Department of Defense, through the Northwestern University Materials Research Center.

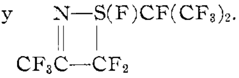
Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida

N-Perfluoroalkyl S-Perfluoroisopropyl Iminosulfur Monofluorides[1]

By R. D. DRESDNER, J. S. JOHAR, J. MERRITT, and C. S. PATTERSON

Received November 9, 1964

The new class of fluorocarbon compounds, named for the first time in the title, involving a –C—N═S—C– bonding arrangement is prepared by reaction of the analogous fluorocarbon iminosulfur difluorides with perfluoropropene over solid powdered CsF at 80–90° in a closed vessel. The reaction appears to proceed slowly *via* the formation of a perfluoroisopropyl carbanion, which as a Lewis base complexes with the acidic sulfur by using its d-orbitals while essentially simultaneously the less basic F^- ion is eliminated to a neighboring defect site. When the reaction was studied with $C_3F_7N{=}SF_2$, one of the by-products that was also isolated and identified was a rather unique compound for which it is impossible, as yet, to account, *viz.*, $C_6F_{13}NS$, probably



$$\begin{array}{ll} \mathrm{N} & \!\!\!\!\text{—}\mathrm{S(F)CF(CF_3)_2} \\ \| & \;\;| \\ \mathrm{CF_3C} & \!\!\!\!\text{—}\mathrm{CF_2} \end{array}$$

Introduction

Although there are many examples of negative ion Lewis bases as attacking species in the general field of fluorine chemistry, the number of examples is more limited in the case of perfluoroalkyl carbanions.[2-6]

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[1] This work was supported by the Advanced Research Projects Agency through the Army Research Office at Durham, N. C. This support is gratefully acknowledged.

(2) W. T. Miller, J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(3) W. T. Miller, W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961).

(4) W. J. Brehm, K. G. Bremmer, H. S. Eleutrio, and R. W. Meschke, U. S. Patent 2,918,501 (1959).

Much of the work reported was performed in solutions of nonaqueous polar solvents. There is no evidence presented to show that reactions were not taking place in slurries. In a recent paper[7] in which an unambiguous study is performed some insight into the nature of carbanion attack is revealed. In this paper, studies involving perfluoroisopropyl carbanion were extended to reaction with a new class of compounds, the fluorocarbon iminosulfur difluorides, $R_fN{=}SF_2$.[8] No solvents were used. The original object in preparing the N-perfluoroalkylated S-perfluoroisopropyl iminosulfur monofluorides, $R_fN{=}S(F)CF(CF_3)_2$, was to determine if they were more "thermally" stable than the parent difluorides. They were not.

Experimental

All the reactions were carried out in a low-pressure reaction vessel constructed from a 500-ml. Hoke stainless steel container adapted to attach a pressure gauge and a valve. The vessel was charged with about 100 g. of CsF which was vacuum dried at about 450° for 24 hr. before each use. Heating of the vessel was carried out in an upright tube-type furnace. Temperatures were determined with a thermocouple inserted in the wall of the furnace.

The SF_4 used for preparing the fluorocarbon iminosulfur difluorides was purchased from the du Pont Company and fractionated to remove SOF_2. The CF_3CN and C_2F_5CN used for the same purpose were purchased from Peninsular ChemResearch of Gainesville, Fla. The sodium thiocyanate used to prepare $CF_3N{=}SF_2$ was purchased as Baker and Adamson C.P. grade.

The perfluoropropene used in this work was purchased from Peninsular ChemResearch and refractionated.

Infrared spectra were determined on a Perkin-Elmer 137B Infracord. N.m.r. spectra were determined on a Varian A-60 spectrometer at 56.4 Mc. CF_3COOH was used as the external standard.

The perfluoromethylethyl and -propyl iminosulfur difluorides were made according to the methods outlined in the literature.[8] In general, it was noted that less drastic conditions were required if the SF_4 used was purified (99%) in contrast to the technical grade purchased. Slightly better yields resulted at somewhat (up to 50°) lower reaction temperatures. Pressures above 235 atm. gave the best results and were achieved by using an excess of SF_4.

$CF_3N{=}S(F)CF(CF_3)_2$.—$CF_3N{=}SF_2$ (41 g., 0.27 mole) and 96 g. (0.64 mole) of C_3F_6 were condensed into the reaction vessel. The system was heated to 83° over a 5-hr. period and maintained at this temperature for 115 hr. During this time interval, the system pressure dropped from 18.5 to 14 atm. and heating was discontinued. The products of the reaction were transferred to a vacuum system and stripped of low boiling components. The materials boiling above 25° were fractionated and several fractions boiling between 62 and 67°, amounting to 50 g., were analyzed by v.p.c. using a 2-m. DNP column. The fraction that manifested the highest (97%) purity boiled between 65.0 and 65.5°. It is estimated from an analysis of each fraction that 43.5 g. of pure product had been made. This amount was equivalent to a yield of 52% assuming all the starting difluoride was used up. As it boiled at −6°, it was in the low boiling fraction which was not separated into its components, although infrared analysis indicated that some amount of starting iminosulfur difluoride was present.

The infrared spectrum of the product determined at 6 mm. pressure in a 5-cm. cell was as follows (cm.$^{-1}$): 1300 (vs) (fairly well-resolved side band), 1265 (vvs), 1215 (s), 1180 (s), 1145 (ms), 1125 (s), 985 (s), 957 (w), 830 (vw), 760 (w), 725 (ms), and 705 (s).

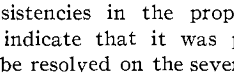
The n.m.r. spectrum of this homolog was as follows (chemical shifts in p.p.m.): CF_3N, −25.1 (2.9); SF, −66.6 (1.0); CF, 92.0 (0.9); $(CF_3)_2C$, −6.3 (5.8).

$C_2F_5N{=}S(F)CF(CF_3)_2$.—$C_2F_5N{=}SF_2$ (36 g., 0.18 mole) and 51 g. (0.34 mole) of C_3F_6 were charged into the reaction vessel and heated slowly to about 85° over a 5-hr. period. The reaction temperature was maintained between 83 and 89° for the next 115 hr. The pressure in the system dropped from 12.2 to 6.9 atm. Again, the material boiling essentially above 25° was fractionated and a series of fractions was obtained boiling between 80 and 83°. These were analyzed by v.p.c. using a DNP column. The purest (96%) fraction boiled between 81.5 and 82.0°. The total quantity of $C_2F_5N{=}S(F)CF(CF_3)_2$ produced was estimated from v.p.c. analyses to be 54 g., equivalent to an 87% yield. This figure is corrected for recovered starting material which boiled at 23°. This product homolog had a density of 1.679 g./ml. at 27° and an $n^{22}D$ of 1.2951.

The infrared spectrum, run at 13 mm. pressure, showed absorptions at the following wave numbers (in cm.$^{-1}$): 1380 (vvw), 1300 (vvs) (side band), 1250 (vvs), 1140 (s), 1110 (vs), 1060 (s), 1030 (vs), 983 (vs), 950 (s), 760 (ms), and 700 (ms). The 1380 cm.$^{-1}$ value could be due to a small impurity.

The n.m.r. spectrum for this homolog is (chemical shifts in p.p.m.): CF_3C, 14.5 (3.0); CF_2N, 17.4 (1.9); SF, −52.3 (1.0); CF, 90.0 (1.0); $(CF_3)_2C$, −8.4 (6.1).

$C_3F_7N{=}S(F)CF(CF_3)_2$. Trial I.—$C_3F_7N{=}SF_2$ (32 g., 0.13 mole) and 46 g. (0.32 mole) of C_3F_6 were condensed into the reaction vessel. The reaction mixture was heated slowly to 112° over a 6-hr. period and maintained at this temperature for 145 hr. The pressure dropped in the interval from 13 to 8.1 atm. The material boiling above 25° was carefully fractionated in a 25-plate spinning-band column; 40 g. of material boiled between 95 and 106° without any flats in the distillation curve. Fractions which were cut arbitrarily were analyzed by v.p.c. The product present in the greatest amount was estimated to amount to 23 g. and later proved to be the so-called desired product, $C_3F_7N{=}SF(i\text{-}C_3F_7)$. However, it was present in no one fraction to an amount greater than 75 mole %. There were at least six other components present, two each of which appeared to amount to 16 mole % of the total. The other components were less well resolved on both a DNP column or a silicone (SF50) oil column. A preparative scale silicone oil column, 16 ft. long of 0.5-in. glass pipe, was used to separate the three major materials. Resolution on the preparative scale column was better at room temperature than it was at any higher temperature up to 85°. After preparative scale separations were complete, a 23-g. fraction and two 7.5-g. fractions were obtained. The large fraction and one of the other two were identified as $C_3F_7N{=}SF(i\text{-}C_3F_7)$ and the cyclic compound



respectively. Inconsistencies in the properties of the third fraction tended to indicate that it was probably a mixture which had failed to be resolved on the several v.p.c. columns on which it was analyzed, as the back side of the appearance peak was suspiciously uneven.

The infrared spectrum for the acyclic derivative (in cm.$^{-1}$) is: 1295 (vs) (side band), 1235 (vs, broad), 1140 (s), 1120 (s), 1095 (m), 1060 (s), 982 (s), 966 (s), 948 (s), 934 (s), 767 (m), 735 (ms), 713 (s), and 697 (s). This spectrum was run at 10 mm. pressure.

The infrared spectrum for the cyclic compound (in cm.$^{-1}$) is: 1760 (ms), 1330 (ms), 1280 (vs), 1220 (vs), 1200 (ms), 1175 (ms), 1125 (s), 1000 (s), 967 (m), 950 (s), 816 (w), 755 (ms), 738 (s), and 716 (s). This spectrum was run at 10 mm. pressure.

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TABLE I

CONDITIONS AND RESULTS OF THE REACTION OF $R_fN{=}SF_2$ AND $CF_3CF{=}CF_2$

	Moles of reactants		Peak reaction temp., °C.	Peak press., atm.	Effective reaction time, hr.	Yield of $R_fN{=}S(F)(i\text{-}C_3F_7)$
	$R_fN{=}SF_2$	C_3F_6				
CF_3	0.27	0.64	83	17	115	52[a]
C_2F_5	0.18	0.34	89	11	120	87
C_3F_7	0.11	0.40	85	14	84	64
C_3F_7	0.13	0.32	112	13	150	48[b]

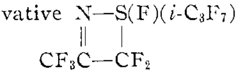
[a] This is a minimum yield not corrected for recoverable $CF_3N{=}SF_2$. [b] In both trials with the propyl derivative  $\begin{array}{l}N\text{—}S(F)(i\text{-}C_3F_7)\\ \| \quad\ | \\ CF_3C\text{—}CF_2\end{array}$ was a product, but more numerous by-products were present in the higher temperature run (called trial I).

TABLE II

THE SIMPLE PROPERTIES AND ELEMENTAL ANALYSES OF THE N-PERFLUOROALKYL S-PERFLUOROISOPROPYL IMINOSULFUR DIFLUORIDES

Compound derivative	Purity, mole %	B.p., °C., ±0.5°	Mol. wt.		F, %		C, %		N, %		S, %	
			Calcd.	Found[a]	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
CF_3	97	65.7	303	306	69.0	69.2	15.8	15.7	4.63	4.72	9.9	10.1
C_2F_5	99	82.3	353	354	70.0	69.6	17.1	17.0	4.0	3.8	9.1	9.2
C_3F_7	95	103.5	403	400	70.8	70.4	17.9	17.9	3.5	3.4	7.9	8.3
$C_6F_{13}NS$	96	100	365	369	67.7	67.1	19.8	19.9	3.8	3.6	8.8	9.1

[a] Obtained by vapor density. A cathetometer was used with higher boiling materials.

The n.m.r. spectrum for the acyclic derivative is (chemical shifts in p.p.m.): CF_3C, 4.8 (3.0); CCF_2C, 52.7 (1.9); CF_2N, 8.6 (2.0); SF, −67.6 (0.9); CF, 91.2 (1.1); $(CF_3)_2C$, −6.6 (6.0).

The n.m.r. spectrum for the cyclic compound is (chemical shifts in p.p.m.): CF_3C, 7.7 (3.0); CF_2, 42.7 (1.9); SF, −45.1 (1.0); CF, 87.0 (0.9); $(CF_3)_2C$, −4.4 (6.0).

Discussion

The S-perfluoroisopropyl iminosulfur monofluorides, $R_fN{=}S(F)CF(CF_3)_2$, were prepared by reaction of the appropriate difluoride with perfluoropropene over dry, powdered CsF in a stainless steel vessel at about 85° for several days. The autogenous pressure varied with time but was in the order of 10 to 15 atm. Table I lists the conditions and yields of several representative reactions when about 0.7 mole (100 g.) of CsF was used.

As indicated in Table I, when the perfluoropropyl iminosulfur difluoride was a reagent, secondary or side reactions resulted in the formation of a number of side products whose boiling points appeared to be very close to that of the main product, complicating the attempts made to separate these substances. Although several of the side products were isolated, only one was successfully identified.

One of the several problems associated with the identification of these new compounds was that the characteristic infrared spectral absorptions associated with the $N{=}SF_2$ system generally found in the 7.20 μ region (1390 cm.$^{-1}$) seemed to have disappeared for the isopropyl derivatives. It was not improbable that the shift had occurred to longer wave length and was obscured by the strong bands in the C—F region which start as low as 1350 cm.$^{-1}$. This hypothesis was checked on the compound $C_6H_5N{=}S(OCH_3)_2$,[9] which had no interfering C—F absorptions, and the N=S absorption was observed at 1283 cm.$^{-1}$. Thus, knowing, *a priori*, where to look with some assurance, it appears that the N=S absorptions for the isopropyl derivatives lie in the range 1279 to 1272 cm.$^{-1}$.

A second problem arose as a result of the n.m.r. spectral splittings attributed to the fluorines in the carbon attached to nitrogen. For the perfluoropropyl and -ethyl compounds, the spectral splitting seemed to be that for a nonequivalent quartet, sometimes associated with a CF_2 group in a four-membered ring. For the perfluoromethyl compound, the so-called quartet was resolved into two doublets, presumably as a result of spin–spin coupling with both the SF and CF fluorines. However, on the basis of the infrared and the n.m.r. data there is no doubt about the acyclic nature of the compounds.

The structure of the substance detected, isolated, and identified as a substantial by-product in the reaction between $C_3F_7N{=}SF_2$ and C_3F_6 in accordance with our best molecular weight and elemental analysis data had the molecular formula $C_6F_{13}NS$ with two less fluorine atoms than the major product by weight, namely $C_3F_7N{=}SF[CF(CF_3)_2]$, $C_6F_{15}NS$. Its n.m.r. spectrum indicated only five kinds of fluorine. The structure of the molecule was constructed from this evidence and certain available infrared evidence. An absorption of 1707 cm.$^{-1}$ can only be associated with a C=C or a C=N unsaturation for the elements available in the compound. Recent data on ring compounds involving C=N absorption in the infrared spectrum as a consequence of ring strain is helpful. For example, heptafluoro-1,3,5-triazacyclohexene absorbs at 1745 cm.$^{-1}$,[10] while a five-membered heterocyclic, heptafluoro-1-azacyclopent-1-ene, absorbed strongly at 1720 cm.$^{-1}$.[11] This trend along with other evidence for structure

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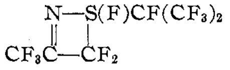
(9) We are most grateful to Dr. V. A. Engelhardt of the E. I. du Pont de Nemours Experimental Station, Wilmington, Del., who kindly provided an infrared spectrum of this material.

(10) J. B. Hynes and L. A. Bigelow, *J. Am. Chem. Soc.*, **84**, 2751 (1962).

(11) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, **84**, 3409 (1962).

seems to be consistent with a cyclic four-membered ring compound, *viz.*



although how a compound with such a structure might result from the reaction involved is far from clear. In the final analysis attack by a perfluoroisopropyl carbanion must have been involved.

Table II lists the simple properties and the analytical data for the various compounds described in this paper.

Acknowledgments.—The authors wish to thank a colleague, Dr. Robert Hanrahan, for the use of preparative scale v.p.c. equipment and Mr. James McCully and Mr. William Blasky for their assistance in the tedious operation of the equipment for separating liquid mixtures. We are also very indebted to Dr. W. S. Brey, another colleague, and his students for obtaining the n.m.r. spectra for the various compounds involved.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Structure of Thiotrithiazyl Nitrate, $S_4N_3NO_3$

BY A. W. CORDES, R. F. KRUH, AND E. K. GORDON

Received November 30, 1964

The structure of thiotrithiazyl nitrate, $S_4N_3NO_3$, shows the $S_4N_3^+$ cation to be cyclic with six nitrogen–sulfur bonds and one sulfur–sulfur bond. The cation is planar within the experimental uncertainties. The nitrogen–sulfur distances are all nearly equal and average 1.55 Å., which suggests a bond order of about two. The sulfur–sulfur distance is 2.06 Å., a value which is a single-bond length. The SSN bond angles are 111°, the NSF angles 119°, the two equivalent SNS angles are each about 152°, and the unique SNS angle is 135°.

Sulfur nitride, S_4N_4, is the parent compound for a large number of varied products which retain from one to all eight of the original sulfur–nitrogen linkages.[1] One of the products, obtained by treating sulfur nitride with gaseous hydrogen chloride in carbon tetrachloride, is the thiotrithiazyl cation, $S_4N_3^+$. The ionic nature of this seven-atom unit is demonstrated by its ability to form a number of salts by simple metathetical reactions in aqueous solution. A structural investigation of the nitrate salt of $S_4N_3^+$ was begun in our laboratory in 1961[2] and a similar study was initiated at about the same time at Heidelberg University in the laboratory of Dr. Johannes Weiss.[3] In 1962 Weiss reported tentative parameters which indicated a cyclic structure for $S_4N_3^+$, but he was not able to ascertain whether the ring was a planar unit. Moreover, an incorrect space group was reported. The present report is an account of our determination confirming the existence of a nearly planar ring.

Experimental

The compound was prepared by dissolving S_4N_3Cl in concentrated nitric acid, and the crystals were obtained directly from this solution by allowing the hot solution to cool slowly. The yellow crystals grow in two forms: plates whose principal faces are (010) or (100), and needles elongated in the *c* direction. Goniometric study indicated holohedral monoclinic symmetry 2/m. The information used for the structural determination was obtained from both varieties. The crystals decompose upon heating or upon prolonged exposure to air.

All of the diffraction measurements were carried out at room temperature using nickel-filtered Cu Kα radiation; 1.540 Å. was used for the wave length of the radiation. The unit cell dimensions, as measured from rotation and Weissenberg photographs, are: $a = 5.84 \pm 0.02$; $b = 10.50 \pm 0.01$; $c = 12.15 \pm 0.01$ Å.; $\beta = 101 \pm 0.3°$. Systematic absences ($h0l$ for $h + l$ odd and $0k0$ for k odd) indicate the space group $P2_1/n$ (general positions: $\pm(x, y, z)$, $\pm(^1/_2 - x, ^1/_2 + y, ^1/_2 - z)$). The density was found by flotation to lie between 1.99 and 2.18 g. cm.$^{-3}$, a value which indicates four molecules per unit cell. The calculated density is 2.13 g. cm.$^{-3}$.

The data which were used to deduce the atomic positions were provided by 113 observed and 27 unobserved $0kl$ reflections and 55 observed and 14 unobserved $hk0$ reflections. Fifteen $0kl$ and eight $hk0$ reflections were not included because of evidence of secondary extinction. These reflections, of high intensity, were omitted from all of the calculations, including the final refinement. The final refinement used a total of 615 three-dimensional data.

The intensities were estimated visually with the aid of a calibrated strip. Because of the uncertainty in the intensity introduced by partial decomposition of the crystal during the measurement, no general correction was made for absorption or for shape of the reflection spot.

Determination of the Structure

Possible y,z coordinates were obtained from the $0kl$ data by a direct determination of phases[4] and by applying the superposition method[5] to the Patterson projection on (100). These two independent approaches agreed in general on the positions of the atoms in the

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[1] For review articles see M. Goehring, *Quart. Rev.* (London), **10**, 437 (1956), or M. Becke-Goehring, *Progr. Inorg. Chem.*, **1**, 208 (1959).

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[3] J. Weiss, *Angew. Chem. Intern. Ed. Engl.*, **1**, 214 (1962).

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