positions and intensities of the visible absorption bands, are all quite in order for a tetrahedral complex.

Thus, on the basis of all the available data, we believe that $[Co(O_2CCF_3)_4]^{2-}$ can be satisfactorily described as a tetrahedral Co(II) complex in the literal structural sense as well as in regard to its electronic structure, in contrast to $Co(NO)_3)_4^{2-}$, where the structure is more nearly an eight-coordinate one with the gross electronic structure parameters merely "mimicking" those of truly tetrahedral complexes as explained previously.[2]

The gradation from an essentially regular dodecahedral structure in some cases through the intermediate case represented by $Co(NO_3)_4^{2-}$ to the extremely deformed, essentially tetrahedral structure found in $Co(O_2CCF_3)_4^{2-}$ is interesting, but at present we are not in possession of any satisfactory explanation.

Acknowledgment.—We thank the MIT Computation Center for generous allotments of time on the IBM 7090 computer.

Contribution from the Department of Chemistry,
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Preparation and Properties of Pentafluorosulfanyliminosulfur Difluoride, $SF_5N{=}SF_2$[1,2]

By ALAN F. CLIFFORD[3] and JAMES WOOD THOMPSON

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The reaction of SF_4 and NSF_3 in the presence of boron trifluoride yields pentafluorosulfanyliminosulfur difluoride, $SF_5N{=}SF_2$. The compound hydrolyzes very slowly with water but very rapidly with aqueous NaOH. It is liquid at −119° and boils at 43°. The structure which has been assigned to the molecule is consistent with mass, infrared, and F^{19} nmr spectral data.

Introduction

Compounds containing iminosulfur difluoride structures have come to be known only in the past 5 years or so. Several organic iminosulfur difluorides have been prepared by treating sulfur tetrafluoride with compounds containing carbon–nitrogen multiple bonds.[4-8] The purpose of this work was to prepare an iminosulfur difluoride with the functional group attached to some element other than carbon.

Experimental Section

Materials and Equipment. Sulfur Tetrafluoride.—Sulfur tetrafluoride (Olin Mathieson Co.) was used without further purification since thionyl fluoride was the only impurity which could be detected in the infrared spectrum of the material.

Potassium Fluoride.—Potassium fluoride (Allied Chemical Corp.) was anhydrous, granular reagent grade and was dried for at least 24 hr at 375°. It was stored in a polyethylene bottle in a desiccator. It was always loaded into the reactor in the drybox.

Boron Trifluoride.—Boron trifluoride (Olin Mathieson Co.) was used without further purification since a trace of SiF_4 was the only impurity which could be detected in the infrared spectrum of the material.

Silver Difluoride.—Silver difluoride (Harshaw Chemical Co.) was technical grade.

Reactors.—Hoke (Cresskill, N. J.) stainless steel cylinders equipped with Hoke Model M327A series needle valves were used for the reaction and for storage of the reaction products of high volatility.

Metal-to-Glass Connections.—Metal-to-glass connections were effected with brass Swagelok (Crawford Fitting Co., Cleveland, Ohio) unions fitted with Teflon ferrules. Vacuum-tight connections were effected with 6-mm o.d. Pyrex tubing and 0.25-in. Swagelok tube fittings. A Teflon tape dope manufactured by the Hercules Chemical Co., Inc. (New York, N. Y.), was applied to all thread fittings before connections were made.

Vacuum System.—An all-Pyrex-glass high-vacuum system was employed for handling the reactants and products. All stopcocks and ground-glass joints were greased or waxed with Kel-F brand 90 grease manufactured by the Minnesota Mining and Manufacturing Co. or with Halocarbon wax manufactured by Halocarbon Products Corp. (Hackensack, N. J.).

Autoclave.—A 150-cc Magne Dash Hastelloy "C" autoclave manufactured by Autoclave Engineers, Inc. (Erie, Pa.), was used for reactions of large volume after first pressure testing at a much higher pressure than the reaction pressure.

Preparation of Thiazyl Trifluoride.[9]—Thiazyl trifluoride was prepared from fluoroformyliminosulfur difluoride[8] by oxidation with silver difluoride. A quantity of SF_2NCOF, 4.44 g, was introduced into a 3-l. flask which had been loaded with 16.5 g of AgF_2 (mole ratio 2:5) and evacuated. The flask and contents were placed in an oven at 38° for 16 hr. The contents were then passed through a −130° trap (*n*-pentane) which removed the NSF_3 while the COF_2 was collected at liquid nitrogen temperature. After several passes of the material in the −130°

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(1) Taken from the thesis submitted by J. W. Thompson to the faculty of Purdue University in partial fulfillment of the requirements for the M.S. degree. Reported at the 3rd International Fluorine Symposium, Munich, Aug 31, 1965.

(2) This research was performed under National Science Foundation Grant No. GP-580.

(3) Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Va.

(4) W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Englehardt, and D. D. Coffman, *J. Am. Chem. Soc.*, **81**, 3165 (1959).

(5) W. C. Smith, C. W. Tullock, R. D. Smith, and V. A. Englehardt, *ibid.*, **82**, 551 (1960).

(6) W. C. Smith, *Angew. Chem.*, **74**, 742 (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 467 (1962).

(7) C. W. Tullock (to E. I. du Pont de Nemours and Co.), U. S. 2,883,422 (1959).

(8) A. F. Clifford and C. S. Kobayashi, *Inorg. Chem.*, **4**, 511 (1965).

(9) A. F. Clifford and J. H. Stanton, to be published.

trap through the *n*-pentane trap, an infrared spectrum[10] and molecular weight were taken as checks of purity. The material was stored in a 75-ml Hoke stainless steel cylinder until needed.

Preparation of Pentafluorosulfanyliminosulfur Difluoride.—Equimolar amounts of NSF_3 and SF_4 were condensed into a 10-ml Hoke stainless steel cylinder and left at room temperature overnight. The pressure was found to be unchanged, and the infrared spectrum showed no peaks not due to the starting materials. The material was condensed back into the reactor and heated to 160° for 12 hr. The reaction mixture was cooled, and again the pressure and infrared spectrum were unchanged. A catalytic amount of CsF was added to the reaction mixture which was heated to 160° for 3 hr. The mixture was cooled and it was found that there was no evidence for reaction. Consequently, the reaction was run for a longer period of time, 24 hr, and at a higher temperature, 200°. Again there was no reaction.

Equimolar amounts of NSF_3, SF_4, and BF_3 (2.7 mmoles) were added to a 10-ml Hoke stainless steel cylinder and heated for 3 hr at 132°. The cylinder was removed from the oven and allowed to cool to room temperature. The material showed a slight decrease in pressure and infrared peaks not due to the starting materials. By cooling the cylinder under running water immediately after taking from the oven, these new peaks increased in their intensity. The material was passed through a −78° trap (Dry Ice–trichloroethylene) which removed most of the $BF_3 \cdot SF_4$ adduct and a small amount of $BF_3 \cdot NSF_3$. The material was then passed through a −119° trap (ethyl bromide) which removed the product and most of the thiazyl trifluoride. Thionyl fluoride, any SiF_4, and some thiazyl trifluoride were then trapped at liquid nitrogen temperature. The contents of the −119° trap consisted of $SF_5N{=}SF_2$ and some NSF_3. The NSF_3 was removed by pumping on the trap while it was held at −119° since at this temperature the product has little vapor pressure while the NSF_3 still has a vapor pressure of 0.001 mm. This method, however, is suited to purifying only very small amounts. Larger amounts were purified by placing a cooled dewar flask around the trap containing the product and passing the material through a −112° trap (1-bromobutane). Most of the product was trapped out and only a small amount was found in the liquid nitrogen trap along with NSF_3. It required many such operations before the infrared spectrum showed no NSF_3 present.

The reactions were run over a range of temperatures, with the temperature of 180° giving the best yield. Even at this temperature, however, the yield was still quite low (3%). The insides of the stainless steel reactors were found to be coated with a yellow solid regardless of the temperature at which the reactions were run. At higher temperatures the amount of yellow solid increased. This solid when exposed to the air turned dark orange and deliquesced. Spot tests indicated that there was iron(III) present, suggesting that the solid was metal fluoride. No elemental sulfur was found after treating some of the solid with CS_2 and then evaporating the CS_2. The Hastelloy autoclave was also observed to have traces of metal fluoride present.

The Properties of $SF_5N{=}SF_2$.—The product is a clear, colorless liquid boiling at 38° (extrapolated) and still liquid at −119°. The molecular weight was determined by the vapor density method and from the molecule-ion peak of the compound in its mass spectrum. By the vapor density method the molecular weight was 208.5, and by mass spectrum, 211. The calculated molecular weight is 211.

The infrared spectrum in the 2–15-μ region was obtained with a Perkin-Elmer Model 137 Infracord spectrometer using a 10-cm NaCl window gas cell. This was used for a constant check on the purity of the sample. The NaCl windows were not etched when the product was pure. The spectrum in the 15–25-μ region was obtained with a Beckman IR5A spectrophotometer equipped with CsBr optics. The cell had KBr windows with a path length of 10 cm.

The vapor pressure measurements were made in the high-vacuum system employing a conventional mercury manometer. The vapor pressure data treated by the least-squares method gave the equation

$$\log P_{\text{mm}} = 7.6948 - 1520T^{-1}$$

The experimental data, given in the order T (°K), vapor pressure (mm), are as follows: 175.5, 0.1; 189.7, 0.6; 209.8, 2.4; 228.1, 10.0; 250.4, 40.0; 273.3, 164.8; and 299.3, 382.4. The pressure of 382.4 mm at 299°K is somewhat greater than the "about 20 cm" at "room temperature" reported by Peacock.[11] The calculated boiling point is 43°. The heat of vaporization calculated from the Clausius–Clapeyron equation is 7.74 kcal/mole. The Trouton constant was calculated to be 24.9.

The Hydrolysis of $SF_5N{=}SF_2$.—Gaseous $SF_5N{=}SF_2$ was introduced into a vessel containing distilled water at room temperature with no fuming or other reactions observed. At the end of a 2-hr period an infrared spectrum recorded some NSF_3, but mostly unreacted $SF_5N{=}SF_2$. The reaction was followed by means of infrared spectra for 4 days with a gradual increase in the NSF_3 content. After 4 days at least half of the $SF_5N{=}SF_2$ was still present. In addition, a new compound appeared with infrared peaks at 1377 and 1360 cm^{-1}, which are in the S=O stretch region. This was not SO_2, for the other peaks characteristic of SO_2 were not present. The intensity of the S(IV)–F peaks decreased while the S(VI)–F remained almost the same. An unsuccessful attempt was made to isolate an intermediate product. It was assumed, however, that the $SF_5N{=}SF_2$ was reacting with water to produce $SF_5N{=}S{=}O$, an assumption which has been confirmed by Peacock,[11] who did not, however, give details of the infrared spectrum. The production of NSF_3 comes from further hydrolysis of $SF_5N{=}S{=}O$, as also confirmed by Peacock. Sulfur dioxide was not detected, for there was an excess of water.

The rate of hydrolysis was found to be greatly increased in basic solution according to the equation

$$SF_5N{=}SF_2 + 10OH^- \longrightarrow SO_3NH_2^- + 7F^- + SO_3^{2-} + 4H_2O$$

The neutralization equivalent was determined by adding an excess of standardized base and back-titrating with standardized hydrochloric acid to a phenolphthalein end point. The titration equivalent for a sample of SF_5NSF_2 was found to be 0.501 mequiv compared with a calculated value of 0.499 mequiv.

Fluorination.—The compound is also remarkably resistant to fluorination, having been recovered largely unchanged after being in contact with AgF_2 at 96–109° for 18 hr.[12]

Other Preparations of $SF_5N{=}SF_2$.—The compound $SF_5N{=}SF_2$ is much more efficiently produced[12] by reaction of NSF_3 with SF_4 in liquid HF or by reaction of SF_5NH_2 with SF_4. These reactions will be described in a subsequent communication.

Results and Discussion

The reactions of thiazyl trifluoride, NSF_3, with sulfur tetrafluoride, SF_4, and of pentafluorosulfanylamine, SF_5NH_2,[12] with sulfur tetrafluoride[13] yield pentafluorosulfanyliminosulfur difluoride, $SF_5N{=}SF_2$. The yield of product from the reaction of thiazyl trifluoride with sulfur tetrafluoride appears to be limited by an unfavorable equilibrium, since, although the reaction appeared qualitatively to run faster at higher temperature, the yield remained around 3%.

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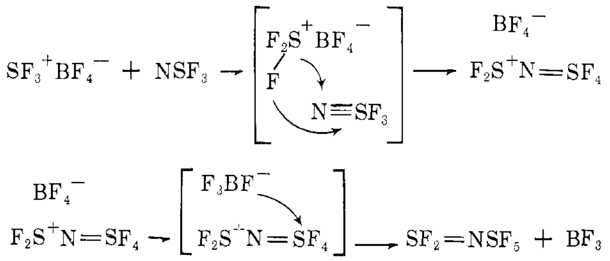
[10] H. Rickert and O. Glemser, *Z. Anorg. Allgem. Chem.*, **307**, 328 (1961).

[11] B. Cohen, T. R. Hooper, and R. D. Peacock, *Chem. Commun.*, 32 (1966).

[12] G. R. Zeilenga, Ph.D. Thesis, Purdue University, 1966.

[13] A. F. Clifford and L. C. Duncan, *Inorg. Chem.*, **5**, 692 (1966).

A possible reaction mechanism is the formation of an addition compound between the sulfur tetrafluoride and the boron trifluoride (postulated by Cotton and George[14] and proved by Seel and Detmer[15] to be $SF_3^+BF_4^-$), followed by the steps



(Alternatively the adduct of BF_3 and NSF_3 may be involved. A similar mechanism can be postulated.) The last intramolecular rearrangement was difficult to predict for the first expected product of the reaction is the isomer $SF_4{=}NSF_3$ (I). No evidence for the presence of isomer I was found, however, the isolated product being only the isomer $SF_5N{=}SF_2$ (II). It is possible, therefore, that there is greater efficiency of the pd–π bonding in the SF_2 group than of d–π bonding in the SF_4 group. Some observations lending credence to this idea are that, although HF readily adds across (and thereby "saturates") S(VI)–N multiple bonds (*e.g.*, HF adds to NSF_3 producing SF_5NH_2[13] and HF adds to $SF_5N{=}CFR$ producing SF_5NHCF_2R,[16] which, when R is C_2F_5, loses HF to give $SF_5N{=}CFCF_2CF_3$ rather than $SF_4{=}NC_3F_7$), HF apparently does not add across S(IV)–N multiple bonds. For example, when $SF_5N{=}SF_2$ is prepared by the reaction of SF_4 and NSF_3 in liquid HF,[12] no SF_5NHSF_3 is isolated and when $CF_3N{=}SF_2$ and $SF_2{=}NCOF$ are mixed with liquid HF,[17] they remain insoluble and unsolvated, although the latter eventually is decomposed.

The mass spectrum (Table I) showing the major peaks above mass 65, obtained on a Hitachi Perkin-Elmer RMU-6A spectrometer, provides strong evidence that the structure of the compound is $SF_5N{=}SF_2$. The heaviest nitrogen-free fragment seen was SF_5^+, which gave the second strongest peak in the spectrum. (The lesser intensity of the SF_5^+ peak relative to SF_3^+ has previously[13] also been observed with SF_5NH_2. It is possible that the presence of the nitrogen atom increases the propensity for loss of a fluorine atom from the SF_5 group (possibly because of its ability to π bond with the SF_4 group remaining) producing $S_2NF_6^+$ or in the latter case $SF_4NH_2^+$ (both of which are observed), which subsequently cleaves, with eventual production of SF_3^+. For isomer I, on the other hand, the heaviest nitrogen-free fragment should be SF_3^+. Outside of the small amount of NSF_3^+ fragment, the heaviest nitrogen-containing fragment was NSF_2^+. Again, isomer II should give NSF_4^+ and a larger amount of NSF_3^+ than was observed as well as the less fluorinated fragments which did appear. Although Peacock[11] reported having used the mass spectrum in the characterization of SF_5NSF_2, no details of the spectrum were given.

TABLE I

MASS SPECTRUM OF $SF_5N{=}SF_2$ (IONIZATION VOLTAGE 75 V)

m/e	Intensity relative to SF_3^+	Ion	*m/e*	Intensity relative to SF_3^+	Ion
213	0.37	$NS^{34}S^{32}F_7^+$	90	1.05	
211	2.77[a]	$NS_2F_7^+$	89	100.0	SF_3^+
194	0.37	$NS^{34}S^{32}F_6^+$	86	0.74	$NS^{34}F_2^+$
192	2.40	$NS_2F_6^+$	84	5.37	NSF_2^+
154	0.61	$NS_2F_4^+$	79	0.31	
129	4.01	$S^{34}F_5^+$	72	1.30	$S^{34}F_2^+$
128	0.93		71	0.31	
127	84.5	SF_5^+	70	24.2	SF_2^+
108	2.68	SF_4^+	67	1.91	$NS^{34}F^+$
103	0.92	NSF_3^+	66	0.43	$N^{15}SF^+$
91	4.56	$S^{34}F_3^+$	65	25.4	NSF^+

[a] Parent peak.

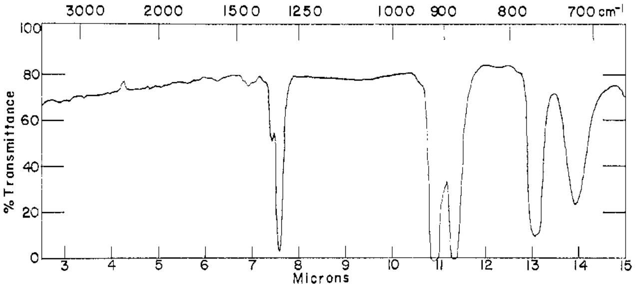


Figure 1.—Infrared spectrum of $SF_5N{=}SF_2$ at 3 mm.

The shouldered peak of the infrared spectrum (Figure 1) at 1313 cm^{-1} was assigned to S=N stretching vibrations since absorption has been found in this region for the organoiminosulfur compounds.[5,8] This does not distinguish between the two isomers, however, since the S=N stretching frequency in the compound $SF_4{=}NCF_3$ has been reported[16] to occur at 1343 cm^{-1}. The doublet at 910 and 879 cm^{-1} was assigned to the S(VI)–F stretch of SF_5, based upon SF_5NH_2[13] and other SF_5 compounds.[18] The doublet at 760 and 714 cm^{-1} was assigned to the S(IV)–F stretch on the basis of the spectra of fluoroformyliminosulfur difluoride[8] and SOF_2.[19] In the far-infrared region (Figure 2) there was a peak at 600 cm^{-1} which is characteristic of all SF_5 compounds.[18] There was also a peak at 469 cm^{-1} which appears to be characteristic of the $=SF_2$ group.[8] All of these peaks except the last were reported by Peacock[11] and are in generally good agreement.

The F^{19} nuclear magnetic resonance measurement (Figure 3) (obtained by Dr. R. F. Merritt of Rohm and Haas Co., for whose assistance we are grateful) showed chemical shifts (measured relative to Freon 11 (CCl_3F)) at −54.8, −84.1, and −87.5 ppm with apparent relative intensities of 2:4:1, respectively, as expected of isomer II, but not of isomer **I**, which should give relative intensities of 1:2:2:2 or possibly

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[14] F. A. Cotton and J. W. George, *J. Inorg. Nucl. Chem.*, **7**, 397 (1958).

[15] F. Seel and O. Detmer, *Z. Anorg. Allgem. Chem.*, **301**, 113 (1959).

[16] C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).

[17] A. F. Clifford and D. Chin, unpublished work.

[18] L. H. Cross, G. Cushing, and H. L. Roberts, *Spectrochim. Acta*, **17**, 344 (1961).

[19] J. I. O'Loane and M. K. Wilson, *J. Chem. Phys.*, **23**, 1313 (1955).

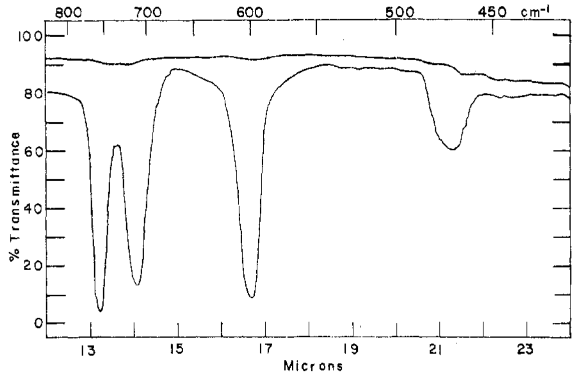

Figure 2.—Infrared spectrum of $SF_5N{=}SF_2$ at 4 mm.

3:2:2. The chemical shift values expressed in ppm relative to CF_3COOH were −108.2, −137.5, and −140.9, respectively. The first resonance, −108.2 ppm, was in agreement with those reported for the iminosulfur difluorides.[3,5] The other two resonances, −137.5 and −140.9 ppm, were also in the reported ranges[20,21] for pentafluorosulfanyl groups. The fine structure was not detected, for the solution was too dilute.

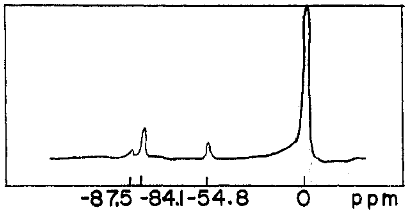

Figure 3.—F^{19} nmr spectrum of $SF_5N{=}SF_2$ 0.2 *M* in reference solvent CCl_3F.

(20) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 340.

(21) C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of Tetraphenylarsonium *cis*-Diaquotetrachlororuthenate Monohydrate[1]

BY TED E. HOPKINS, ALLAN ZALKIN, DAVID H. TEMPLETON, AND MARTYN G. ADAMSON

Received March 18, 1966

X-Ray diffraction study of a single crystal of $(C_6H_5)_4AsRuCl_4(H_2O)_2 \cdot H_2O$ showed that it is monoclinic with a = 15.059, b = 16.711, c = 10.996 A, β = 99.88°, D_x = 1.619 g cm^{-3}. The space group is $P2_1/n$ and there are four formula units per unit cell. The ruthenium is surrounded by an octahedron composed of the four chlorine atoms and two water molecules. A *cis* configuration was found for the waters in the octahedron. The average Ru–O and Ru–Cl distances are 2.12 and 2.34 A. An unsymmetrical configuration was found for the tetraphenylarsonium ion, with an average As–C bond length of 1.91 A.

Introduction

In the course of a series of studies of aqueous ruthenium species by Professor Connick and others at this laboratory, a number of ruthenium salts have been prepared. We have determined the crystal structure of a cesium aquopentachlororuthenate[2a] and of a hexachlororuthenate.[2b] The diaquochloro complex is interesting because of the possibility for *cis–trans* isomers. When it was found that single crystals of the complex could be obtained using the tetraphenylarsonium cation, the structure determination was undertaken to determine the configuration of the ruthenium complex.

Experimental Section

A solution of chlororuthenate species containing a high proportion of the complex ion $RuCl_4(H_2O)_2^-$ was prepared by shaking a solution of 0.1 *M* ruthenium(III) in 2.5 *M* hydrochloric acid with clean mercury and allowing the Ru(III) solution to stand over the mercury for several hours. After the solution was separated from the mercury, it was filtered and sufficient aqueous tetraphenylarsonium chloride solution (0.3 *M*) was added, dropwise with stirring, to give equimolar amounts of $As(C_6H_5)_4^+$ and Ru(III). On standing at 0° for 48 hr, the solution yielded a number of fairly large ruby-red prisms which were collected on a filter pad, washed well with ice-cold water, and finally dried over Anhydrone in an evacuated desiccator.

The nature of the anion in this salt was shown to be exclusively one isomer of the complex. This was done by carrying out ion-exchange and spectral analysis on a freshly prepared solution of the salt in 1 *M* hydrochloric acid at 0°. A study of the aqueous complexes will be reported elsewhere.[3,4]

The Weissenberg technique was used for preliminary determination of the space group and cell dimensions. For taking the data, a single crystal, roughly cubic, 0.15 × 0.17 × 0.18 mm, was mounted for rotation around the b axis. Cell dimensions and intensities were measured with a General Electric XRD-5 diffractometer equipped with a scintillation counter, a pulse-height discriminator, and a quarter-circle Eulerian cradle goniostat. A molybdenum tube was used, operated at 50 kv and 20 ma, with a Zr filter at the receiving slit. For Mo $K\alpha_1$, λ is 0.70926 A.

A graph of the background was prepared for various values of χ and ϕ as a function of 2θ. Typical values were 30, 15, 11, and 4 counts/sec for 2θ = 4, 6, 11, and 21°. For $2\theta > 22°$, the back-

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) (a) T. E. Hopkins, A. Zalkin, D. H. Templeton, and M. G. Adamson, *Inorg. Chem.*, **5**, 1431 (1966); (b) to be published.

(3) D. A. Fine, Ph.D. Thesis, University of California at Berkeley, 1958.

(4) M. G. Adamson and R. E. Connick, to be published.