CONTRIBUTION FROM THE CORPORATE RESEARCH LABORATORIES,
ALLIED CHEMICAL CORPORATION,
MORRISTOWN, NEW JERSEY 07960

A Simple Method for Preparing Chlorine Fluorosulfate

BY C. V. HARDIN, C. T. RATCLIFFE, L. R. ANDERSON, AND W. B. FOX

Received February 9, 1970

A facile, straightforward method has been discovered for the synthesis of chlorine fluorosulfate, and its infrared spectrum has been recorded for the first time.* Thus, we have observed a nearly quantitative yield of chlorine fluorosulfate to be the only product resulting from the room temperature reaction of chlorine monofluoride with sulfur trioxide

$$ClF + SO_3 \longrightarrow ClOSO_2F$$

The previously reported preparation of this compound required heating peroxydisulfuryl difluoride, a substance which is not readily available, with an excess of chlorine under pressure and at 125° for 5 days.[1]

Experimental Section

Apparatus.—Reactions were carried out in 100-cc glass Fischer-Porter pressure vessels equipped with Hoke needle valves. A conventional Monel vacuum line equipped with Kel-F traps was used for handling and purifying volatile materials.

The infrared spectrum of chlorine fluorosulfate was recorded in the 2.5–15-μ region with a Perkin-Elmer Model 137B Infracord spectrophotometer. An 8.8-cm Monel gas cell equipped with AgCl windows was well passivated with chlorine trifluoride before the spectrum was recorded. A Consolidated Engineering Corp. 21-103 mass spectrometer operating at 70 eV was used to record the mass spectrum. The ^{19}F nmr spectrum was determined with an A56-60 Varian spectrometer operating at room temperature.

Reagents.—Chlorine monofluoride (Ozark-Mahoning Co.) and sulfur trioxide (Sulfan-B, Allied Chemical Corp.) were used as received without further purification.

Preparation of Chlorine Fluorosulfate.—A sample of SO_3 (1.040 g; 12 mmol) was syringed into a dry glass reactor under inert atmosphere conditions. After the vessel had been cooled to −196° and evacuated, a sample of ClF (0.880 g; 16.3 mmol) was condensed into the reactor. The reaction mixture was allowed to warm slowly to room temperature with periodic agitation and was observed to form a bright yellow liquid. Volatile impurities were removed under dynamic vacuum at −80° leaving chlorine fluorosulfate (1.695 g; 11.7 mmol) in the reaction vessel, a 97.3% yield based on SO_3. The product was identified by comparison of its ^{19}F nmr and mass spectra with that previously recorded, as well as by its elemental analysis. *Anal.* Calcd for $ClOSO_2F$: Cl, 26.38; S, 23.82; F, 14.12. Found: Cl, 28.43; S, 22.10; F, 12.43. The analytical results varied somewhat from the theoretical values due to small amounts of oxides of chlorine. Attempts to remove these impurities were fruitless since repeated fractionations resulted only in increased decomposition of the $ClOSO_2F$.

Results and Discussion

The reaction of fluorine with sulfur trioxide produced fluorine fluorosulfate, the first sulfur compound to contain an oxygen–halogen bond.[2] More recently, a number of compounds containing the oxygen–chlorine functional group were prepared in this laboratory. These new hypochlorites were synthesized through the catalyzed addition of chlorine monofluoride across either the C=O bond of various fluoroketones or the S=O bond of thionyl tetrafluoride.[3]

The present reaction represents a modification and extension of these procedures to include the addition of chlorine monofluoride across the sulfur–oxygen double bond of sulfur trioxide to produce chlorine fluorosulfate. Here, as in the chlorine monofluoride reactions cited above, the addition is unidirectional and leads to the formation of an O–Cl bond. The alternate product, $FOSO_2Cl$, can be ruled out on the basis of the ^{19}F nmr chemical shift and the mass spectral cracking pattern.

The ^{19}F nmr spectrum, which is in close agreement with that obtained by previous workers, consists of a single resonance at −34.0 ppm relative to $CFCl_3$ as an external standard.

TABLE I
MASS SPECTRUM OF $ClOSO_2F$[a]

m/e	Rel abund[b]	Assignment
134	57.91	$ClOSO_2F^+$
118	0.004	$ClSO_2F^+$
99	0.06	OSO_2F^+
83	100.00	SO_2F^+
80	29.98	SO_3^+
67	10.80	FSO^+
64	16.11	SO_2^+
51	93.67	ClO^+
48	31.28	SO^+
35	81.75	Cl^+

[a] Also present as minor impurities were SiF_3^+, HCl^+, Cl_2^+, and Cl_2O^+. [b] Includes isotopic contributions.

The mass spectrum is of interest because several fragments, including an intense parent ion, were observed which had not been reported previously.[1] The discrepancy can be explained, however, since the molecular ion peak and complete cracking pattern were obtained only after extensive conditioning of the probe chamber with a freshly prepared sample of chlorine fluorosulfate. The cracking pattern shows the expected fragmentation for the structure of $ClOSO_2F$.

The infrared spectrum (Figure 1) was recorded only after great difficulty due to the chemical reaction of chlorine fluorosulfate with the cell windows. After the Monel cell was conditioned periodically with chlorine trifluoride, a sample of $ClOSO_2F$ could be maintained for sufficient time for an infrared scan without decomposition. The bands at 1490 and 1250 cm^{-1} are assigned to the expected asymmetric and symmetric S=O stretching frequencies, respectively,[4] while the absorption at 850 cm^{-1} is due to the S–F stretch. The absorption at 700 cm^{-1} is in the region of the O–Cl

---

* NOTE ADDED IN PROOF.—Subsequent to submission of this paper, similar results were reported by C. J. Shack and R. D. Wilson, *Inorg. Chem.*, **9**, 311 (1970).

(1) W. P. Gilbreath and G. H. Cady, *ibid.*, **2**, 496 (1963).

(2) F. B. Dudley, G. H. Cady, and D. F. Eggers, *J. Amer. Chem. Soc.*, **78**, 290 (1956).

(3) (a) D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *Chem. Commun.*, 1564 (1968); (b) D. E. Young, L. R. Anderson, and W. B. Fox, *J. Amer. Chem. Soc.*, in press.

(4) E. A. Robinson, *Can. J. Chem.*, **39**, 247 (1961).

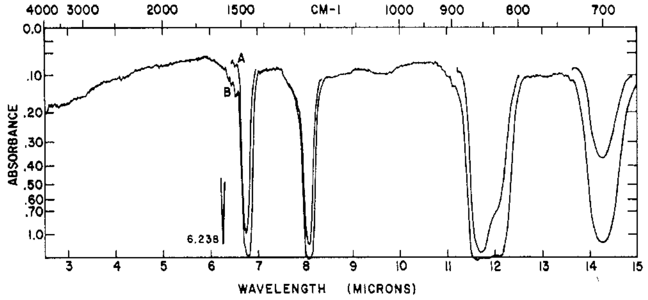

Figure 1.—Infrared spectrum of chlorine fluorosulfate: A, 8 mm; B, 30 mm.

stretching frequencies observed in alkyl hypochlorites[3a,5] and in chlorine monoxide[6] but cannot be definitely assigned.

Acknowledgment.—We wish to thank Mr. E. R. McCarthy for the mass spectral study and Mrs. R. Juurik-Hogan for analytical assistance.

(5) R. Fort, J. Favre, and L. Denivelle, *Bull. Soc. Chim. Fr.*, 543 (1955).

(6) K. Hedberg, *J. Chem. Phys.*, **19**, 509 (1951).

CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Mössbauer Effect and Infrared Investigation of the Black Roussinate Ion [$\mathrm{Fe_4S_3(NO)_7^-}$]

BY E. KOSTINER, J. STEGER, AND J. R. REA

Received February 9, 1970

The structure of the cesium salt of the black Roussinate ion was determined by X-ray diffraction a number of years ago.[1] The structure of the $\mathrm{Fe_4S_3(NO)_7^-}$ ion can be described as a tetrahedral arrangement of iron atoms with sulfur atoms "bridging" three of the faces of the tetrahedron (Figure 1). The apical iron ($\mathrm{Fe_I}$) is bonded to one nitrosyl group at a distance of 1.57 ± 0.04 Å while the other three iron atoms ($\mathrm{Fe_{II}}$) each form bonds to two nitrosyl groups with an average $\mathrm{Fe_{II}}$–N distance of 1.67 ± 0.04 Å. In addition the $\mathrm{Fe_I}$ atom is bonded to three sulfur atoms and forms bonds (at an average distance of 2.70 ± 0.02 Å) with the three $\mathrm{Fe_{II}}$ atoms and each $\mathrm{Fe_{II}}$ atom is bonded to two sulfur atoms and to the $\mathrm{Fe_I}$ atom. The average $\mathrm{Fe_{II}}$–$\mathrm{Fe_{II}}$ distance is 3.57 ± 0.01 Å, implying no bonding interaction between these atoms.[2]

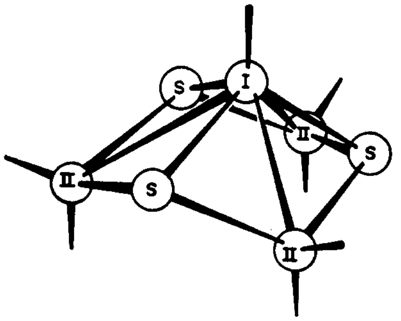

Figure 1.—The $\mathrm{Fe_4S_3(NO)_7^-}$ ion. I is the apical iron atom; II, the other three; for clarity nitrosyl groups are indicated by a line.

Bonding in this molecular ion can be satisfactorily explained either by classical valence bond theory or by using simple molecular orbital theory.[1] The X-ray structure determination confirms the presence of two nonequivalent iron atoms: $\mathrm{Fe_I}$, having C_{3v} symmetry, and $\mathrm{Fe_{II}}$, having C_s symmetry, in the ratio of 1:3.

The only reported Mössbauer-effect data[3] for a Roussin's black salt (the sodium salt—the alkali metal and ammonium salts are isomorphous[1]) show the presence of a doublet characteristic of covalently bonded iron atoms (isomer shift: +0.327 mm/sec, corrected relative to sodium nitroprusside; quadrupole splitting: 0.872 mm/sec, at 25°). These data indicate that there is one type of iron atom present, in disagreement with the X-ray diffraction data. Interestingly enough, these published Mössbauer data show that the width of the resonance absorption lines (full width at half-maximum) *increases* from 0.297 to 0.360 mm/sec on lowering the temperature from 25 to −125°. Although the authors do not comment on this, it seemed suggestive that this broadening was the result of the overlap of two sets of quadrupole split peaks, the Mössbauer parameters of which displayed different temperature dependencies. It was thought that by further cooling it would become possible to resolve the data into the two sets of peaks indicated by the crystallographic investigation. Furthermore, infrared data were obtained to identify the presence (or absence) of bridging nitrosyl groups.

Experimental Section

$\mathrm{NH_4Fe_4S_3(NO)_7 \cdot H_2O}$ was prepared from $\mathrm{FeSO_4 \cdot 7H_2O}$ and ammoniacal $\mathrm{H_2S}$ according to the method of Pawel.[4] *Anal.* Calcd for $\mathrm{NH_4Fe_4S_3(NO)_7 \cdot H_2O}$: N, 19.81; H, 1.07; S, 17.00; Fe, 39.49. Found: N, 18.99; H, 1.20; S, 16.82; Fe, 38.56.

Infrared spectra were taken in potassium bromide pellets on a Perkin-Elmer Model 521 spectrometer and in tetrahydrofuran solution on a Perkin-Elmer Model 337 spectrometer.

The iron-57 Mössbauer effect was measured with a Model NS-1 Mössbauer spectrometer (Nuclear Science and Engineering Corp., Pittsburgh, Pa.) operating in the constant-acceleration mode. The 14.4-keV γ radiation from a source of cobalt-57 diffused into palladium was detected with a gas proportional counter and collected with a 400-channel analyzer (Nuclear Chicago Corp., Chicago, Ill.) operating in time sequence scaling mode. The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec.[5] Isomer shifts were reported with respect to the zero position of this standard. Sample thickness was 20 mg/cm^2 (corresponding to 8 mg of Fe/cm^2). The data were reduced by a computer program which performed a nonlinear least-squares fit to the product of a series of resonant absorption peaks having

---

(1) G. Johansson and W. H. Lipscomb, *Acta Crystallogr.*, **11**, 594 (1958).

(2) Bond distances taken from ref 1.

(3) W. Kerler, *et al.*, *Z. Phys.*, **173**, 321 (1963).

(4) Reported in "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, G. Brauer, Ed., Ferdinand Enke Verlag, Stuttragt, 1962; English translation, P. G. Stecher, Ed., Academic Press, New York, N. Y., 1965.

(5) R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.*, **178**, 523 (1969).