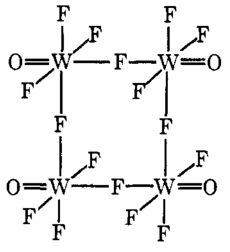
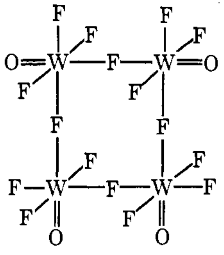
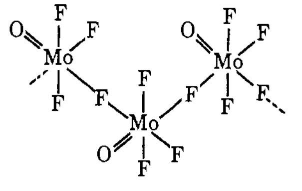

IV


V

pending on the choice of space group C2, Cm, or C2/m. Since none of these structures has a strict mirror plane or twofold axis that contains diagonal tungsten atoms, a disorder, and hence the presence of a pseudosymmetry element, has to be postulated in each case. We prefer structure II on the grounds that it is the structure most likely to disorder in that it is based on a square whereas structures V and VI we estimate to contain a rectangle and trapezoid of tungsten atoms, respectively.

The apparent W–F bridge distance, where the fluorine atom is placed at a position corresponding to the average of structures II and III, can be readily assessed from the structure of $MoOF_4$,[5] assuming that Mo–F and W–F distances will be essentially the same. The structure of $MoOF_4$ is different from that found for WOF_4 in that it forms infinite chains rather than discrete tetrameric units. However, the essential features of the heavy-atom environment are the same as shown in VI. The average of the two independent Mo–F bridge distances (1.96 and 2.27 Å) in this asymmetrically bridged structure is 2.11 Å, the value observed for bridge bonds in the tungsten compound. The hypothesis of the disordered structure was then tested using the published structure factor amplitudes. Two models were tested: (a) the ordered oxygen-bridge structure I and (b) an average of structuring II and III with two independent half-weight fluorine atoms in each bridge, the terminal in-plane atoms each being treated as a single atom comprising half oxygen and half fluorine. Both models were restricted to isotropic refinement and were refined in space group C2/m using scattering factors[6] that included the real and imaginary components of anomalous dispersion[7] and the weighting scheme of Edwards and Jones.[1] In model (b) only one half-weight fluorine was refined in each cycle because of the resolution limits of the data set and naturally high correlation coefficients. Both models refined to R factors 0.126 (defined by $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). The refinement of the disordered model produced asymmetric bridges with individual tungsten–fluorine distances 2.04 (7) and 2.19 (7) Å (average values, standard deviation in parentheses). The other parameters were not significantly different from those already published. The X-ray data do not allow the rejection[8] of the ordered model I. This is not surprising in view of the quality of the data used and the relative insensitivity of the structure factors to small changes in the light atoms when a third-row transition metal is present.


VI

Since the X-ray data do not favor either model, the choice must be made on the basis of other evidence. In this case the spectroscopic evidence[2] and the structural arguments presented here favor a fluorine-bridged structure, and of the fluorine-bridged structures, we find II to be the most attractive.

Acknowledgment.—We thank the National Research Council of Canada for its financial support.

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Selenium Chloride Pentafluoride

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The existence of SF_5Cl has been known[1] for some time, while TeF_5Cl has been reported[2] more recently. However, no report concerning the preparation of the intermediate member of the S–Se–Te triad, SeF_5Cl, has appeared. Since the best synthetic routes[3] to SF_5Cl involve chlorination of sulfur fluoride substrates and since this reaction had been found to be enhanced by added alkali metal fluorides,[4] this technique was applied to the formation of SeF_5Cl. We wish now to report the synthesis and characterization of this new compound.

Experimental Section

Apparatus and Materials.—The equipment used in this work has been described[5] and was supplemented with a Perkin-Elmer Model 457 Infracord and a 10-cm, stainless steel infrared cell fitted with AgBr windows. Details concerning the preparation or treatment of ClF, $ClSO_3F$, and CsF have been given.[5] Additional materials were purchased and used as received.

SeF_4.—Selenium tetrafluoride was first prepared from Se powder and ClF according to Pitts and Jache.[6] Later it was determined that ClF_3 performed equally well in this reaction, thereby circumventing the need to prepare ClF. Typically, a prepassivated 30-ml stainless steel cylinder was loaded with Se powder (14.2 g-atoms) in the drybox. Chlorine trifluoride (20.3 mmol) was added at −196° from a vacuum line and the cylinder allowed to warm slowly to ambient temperature where it was maintained for 1 day or until needed. Vacuum fractionation through U traps cooled to −30, −78, and −196° furnished SeF_4 (12.3 mmol) in the highest temperature trap. The purity and identity of the SeF_4 were verified by its vapor pressure[6] and infrared spectrum.[7] Based on the equation 3Se + $4ClF_3$

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$\rightarrow 3SeF_4 + 2Cl_2$, the yield was 87%, a value comparable to that found for ClF reactions.

SeF_5Cl.—Selenium chloride pentafluoride was prepared by first forming the solid complex $CsSeF_5$ from CsF and SeF_4.[8] Weighed samples of the complex were placed in prepassivated cylinders and $ClSO_3F$ was added at −196°. After warming to room temperature for several hours or more, the volatile products were separated by fractional condensation at −95, −112, and −196°. Unreacted $ClSO_3F$ was retained at −95° while byproducts and impurities such as ClF, $FClO_2$, and Cl_2 passed into the trap cooled to −196°. Pure SeF_5Cl was found in the −112° fraction. From 4.50 mmol of $CsSeF_5$, 4.13 mmol of SeF_5Cl was obtained, corresponding to a yield of 91.7% for the equation $CsSeF_5 + ClSO_3F \rightarrow CsSO_3F + SeF_5Cl$. The presence of uncomplexed CsF in the salt does not inhibit the formation of SeF_5Cl directly but does result in the loss of some $ClSO_3F$ by reaction to form ClF.[5]

Because the system $CsF–SF_4–ClF$ was very effective[4] in producing SF_5Cl, it was expected that $CsF–SeF_4–ClF$ would behave similarly. Such was not the case and unreacted ClF was always fully recoverable after 1 day or several weeks in contact with $CsSeF_5$. However, in the course of preparing SeF_4 from Se and ClF or ClF_3, it was found that excesses of the chlorine fluorides gave detectable yields of SeF_5Cl. To determine the extent of this reaction, 4.19 mmol of SeF_4 and 4.21 mmol of ClF were placed in a 10-ml stainless steel cylinder and kept at ambient temperature for 8 days. Separation of the products by fractional condensation led to the recovery of unreacted SeF_4 and ClF (1.45 mmol of each), as well as trace amounts of SeF_6 and Cl_2. The main product was SeF_5Cl (2.62 mmol), representing a 95% yield based on the SeF_4 that had reacted. With ClF_3, up to 10% yields of SeF_5Cl were obtained but always accompanied by much greater amounts of SeF_6. Thus the direct reaction of SeF_4 and ClF affords an alternate, albeit less efficient, route to SeF_5Cl.

Properties of SeF_5Cl.—Selenium chloride pentafluoride is colorless as a gas, liquid, or solid. It is stable at ambient temperature when stored in clean, dry, passivated stainless steel cylinders. However, contact with glass always resulted in significant decomposition. Even glassware suitably dry and otherwise prepared for the manipulation of ClF_3 did not serve for handling SeF_5Cl. It seems likely that this property hindered the earlier discovery of this compound.

Analysis.—A 0.2001-g sample of SeF_5Cl was hydrolyzed with excess standardized NaOH solution in a glass ampoule fitted with a Teflon Fischer–Porter valve. Fluoride, selenium, and base consumption were determined as reported by Smith and Cady.[9] Fluoride was also determined by the usual thorium nitrate titration. The amount of base consumed was calculated, assuming the hydrolysis equation $SeF_5Cl + 8OH^- \rightarrow SeO_4^{2-} + 4H_2O + 5F^- + Cl^-$. *Anal.* Calcd for SeF_5Cl: Se, 37.71; F, 45.37; OH^- consumed, 8.00 equiv/mol. Found: Se, 37.98; F, 45.18; OH^- consumed, 7.82 equiv/mol.

Molecular Weight.—The molecular weight of the compound as determined by vapor density, assuming ideal gas behavior, was 208 (calcd 209.5).

Vapor Pressure, Boiling Point, and Melting Point.—The vapor (sublimation) pressures of SeF_5Cl over the temperature range −79 to +3° are as follows [T (°C), P (mm)]: −78.7, 6; −64.4, 19; −45.3, 66; −32.2, 142; −23.0, 220; 0.0, 630; 3.5, 729. The pressure–temperature relationship is described by the equation $\log P_{\text{mm}} = 7.779 - 1360/T°\text{K}$. The normal boiling point calculated from the equation is 4.5°, with a heat of vaporization of 6.22 kcal/mol and a Trouton constant of 22.4. Under its own vapor, the compound melts at −19°. Since part of the pressure–temperature data given are below the melting point, it is actually a sublimation pressure and not a vapor pressure. However, pressure values obtained above and below the melting point were nearly on the same line, indicating little difference in the heats of sublimation and vaporization and consequently a very low heat of fusion.

Infrared Spectrum.—The infrared spectrum of SeF_5Cl in the range 4000–250 cm^{-1} shows several absorptions with the most prominent ones occurring at 745 (vvs), 440 (vs), 420 (s), 385 (w), and 335 cm^{-1} (m). The two highest frequencies and the strongest bands noted are comparable to those of bands of similar intensity and position in related hexacoordinate selenium fluorides. Thus, the two strongest bands for SeF_6[10] occur at 780 and 430 cm^{-1} and for SeF_5OF[11] at 750 and 422 cm^{-1}. That these bands are typical of the SeF_5 group is shown by their presence in a series of substituted SeF_5 compounds.[11] A detailed analysis of the vibrational spectrum of SeF_5Cl is in progress.[12]

Nuclear Magnetic Resonance Spectrum.—The ^{19}F nmr spectrum of SeF_5Cl is shown in Figure 1. It is an AB_4 spectrum and resembles that of SF_5Cl[13] so closely as to be virtually identical. The reported[13] chemical shifts for SF_5Cl when converted to a $CFCl_3$ reference point are −62.3 and −125.8 ppm, respectively, for the axial and equatorial fluorines. For SeF_5Cl, the corresponding values taken from Figure 1 are −71.3 and −132.0 ppm. The only part of the spectrum of SeF_5Cl not identical with the SF_5Cl example is the appearance of the small satellite lines due to $^{77}Se–^{19}F$ coupling. The observed coupling constant of 629 Hz is furthermore comparable to selenium–fluorine coupling in compounds which contain a chlorine bonded to the selenium central atom as in SeOFCl, where a value of 647 Hz was reported.[14]

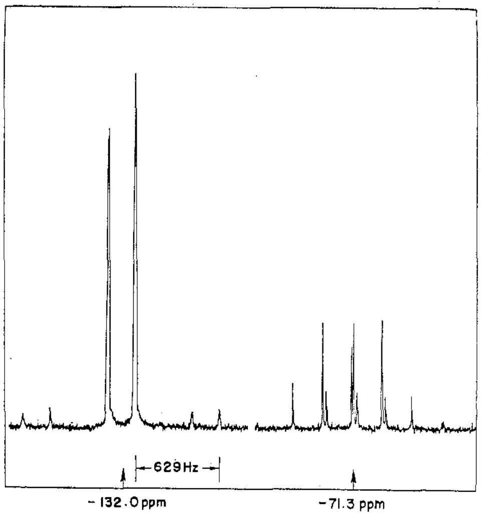

Figure 1.—The ^{19}F nmr spectrum of SeF_5Cl.

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A New Cyclotriphosphazene from a Ring-Closure Reaction

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Considerable work has been done on exchange reactions involving tris(dimethylamino)phosphine with