(c) dissociation of the successor complex

$$[Cr^{II}SCNCr^{III}]^{4+} \rightleftharpoons Cr^{2+} + CrNCS^{2+} \qquad K_3$$

It can readily be shown that

$$(k^{SCN}k^{NCS})^{1/2} = (K_1^{SCN}K_1^{NCS})^{1/2}(k_2^{SCN}k_2^{NCS})^{1/2}$$
$$= (K_1^{SCN}K_1^{NCS})^{1/2}[k_2^{CNS}(K_2^{SCN})^{1/2}k_2^{CNS}(K_2^{NCS})^{1/2})]^{1/2}$$
$$= (K_1^{SCN}K_1^{NCS})^{1/2}k_2^{CNS}$$

where k_2^{CNS} is the hypothetical rate constant for electron transfer with zero free energy change in a thiocyanate-bridged intermediate. It seems reasonable to assume that this rate constant is equal to the rate constant for electron transfer within the symmetrical azide-bridged intermediate, *i.e.*, that $k_2^{CNS} = k_2^{NNN}$.[15] Because $k^{NNN} = K_1^{NNN}k_2^{NNN}$, it follows that

$$\frac{k^{NNN}}{(k^{SCN}k^{NCS})^{1/2}} = \frac{K_1^{NNN}}{(K_1^{SCN}K_1^{NCS})^{1/2}}$$

Since K_1^{NNN} and K_1^{SCN} both involve formation of a N–Cr^{II} bond, it seems likely that they will be quite similar. Hence k^{NNN} will be equal to $(k^{SCN}k^{NCS})^{1/2}$ only if $K_1^{SCN} = K_1^{NCS}$. The experimental data indicate that $K_1^{SCN}/K_1^{NCS} \approx 7 \times 10^3$. This value seems reasonable and indicates that chromium(II) is behaving as a hard metal center toward azide and isothiocyanate.[16] Inspection of Table II suggests that iron(II), too, is acting as a hard metal center in the $(NH_3)_5CoX^{2+} + Fe^{2+}$ reactions.

In the four systems presented in Table II the ratio of k^{SCN}/k^{NCS} is of the order of 10^4–10^5 in all but the series of reactions of vanadium(II) with $(NH_3)_5CoX^{2+}$ where it is 10^2. This comparison supports the view that the reaction of vanadium(II) with $(NH_3)_5CoSCN^{2+}$ (and probably also the reaction of vanadium(II) with $CrSCN^{2+}$) is limited by the rate of water replacement on vanadium(II)[4,17,18] in contrast to the other systems where the rate-determining step is that of electron transfer. The similarity in the rate constants for the oxidation of vanadium(II) by $CrSCN^{2+}$ and by $(NH_3)_5CoSCN^{2+}$ is particularly striking in view of the large difference in the driving force for the two reactions. This similarity provides further evidence for the interpretation that the rates of these reactions are primarily controlled by the rate of loss of a water molecule coordinated to the vanadium(II).[4,17]

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(15) The assumption that $k_2^{CNS} = k_2^{NNN}$ is supported by the observation that k^{NCS}/k^{NNN} is about unity for outer-sphere reactions. See, for example, ref 4.

(16) For comparison with the value of K_1^{SCN}/K_1^{NCS} estimated above, it may be noted that the ratio of the equilibrium constants for the reactions $Cr^{3+} + NCS^- \rightleftharpoons CrNCS^{2+}$ and $Cr^{3+} + SCN^- \rightleftharpoons CrSCN^{2+}$, which is equal to the equilibrium constant for the isomerization reaction $CrSCN^{2+} \rightleftharpoons CrNCS^{2+}$, is 3×10^5 at 25° and 1.0 *M* ionic strength. Evidently the preference for bonding to nitrogen rather than to sulfur is much more marked for chromium(III) than for chromium(II). This conclusion is not unexpected since a Cr^{3+} ion is almost certainly harder than a Cr^{2+} ion.

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trans-Bis(fluoroxy)tetrafluoroselenium [$SeF_4(OF)_2$]

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Fluoroxypentafluoroselenium, SeF_5OF, has been obtained in high yield by the action of fluorine upon seleninyl fluoride, $SeOF_2$, in the presence of potassium fluoride catalyst.[1] While refining the principal product by fractional codistillation, it was observed that a small amount of another compound was present which had a longer retention time than SeF_5OF. By combining the material from several preparative runs, a sufficient amount of the new compound was obtained to allow its identification as *trans*-bis(fluoroxy)tetrafluoroselenium. It is possible that the compound resulted from the action of fluorine upon potassium fluoroselenite, $KSeO_2F$, which could have been formed by the hydrolysis of some $SeOF_2$ and subsequent reaction of the SeO_2 with the potassium fluoride catalyst. The reaction of $KSeO_2F$ with fluorine at −78° was later shown to be a method for the preparation of $SeF_4(OF)_2$.

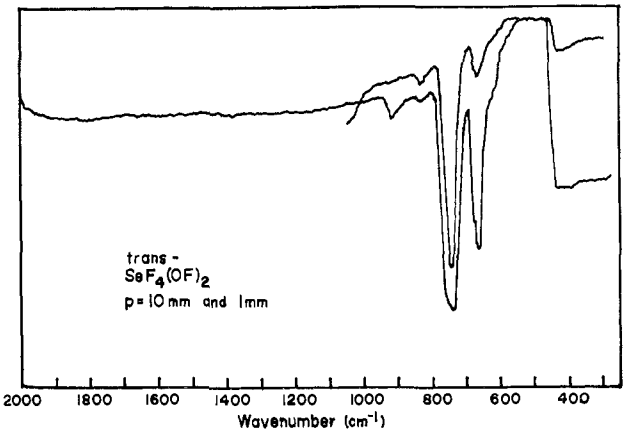

Figure 1.—Infrared spectrum of $SeF_4(OF)_2$.

Preparations

$KSeO_2F$.—Potassium fluoroselenite, $KSeO_2F$, was prepared using a method similar to that described by Paetzold and Aurich.[2] Equimolar quantities of potassium fluoride and selenium dioxide were mixed and heated until molten under a stream of nitrogen in a nickel crucible. A small stainless steel spatula was placed in the salt to facilitate removal after cooling. The crucible was then placed in a desiccator and allowed to cool. The salt was powdered in a mortar before use and was handled in a dry bag.

$SeF_4(OF)_2$.—Approximately 1.1 g of powdered potassium fluoroselenite was placed in a Hoke 4HS30 stainless steel sampling cylinder fitted with a brass valve having a stainless steel needle. A 10-mmol quantity of fluorine was then condensed into the cylinder. The liquid nitrogen was then removed from the dewar vessel surrounding the cylinder, and the cylinder was allowed to

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warm slowly until its temperature reached −78°, at which time the dewar vessel was filled with Dry Ice. After about 12 hr at −78°, the cylinder was cooled to −183° and excess fluorine was removed. The product was then codistilled[3] to permit isolation of $SeF_4(OF)_2$. In a typical run the product consisted of 0.2 mmol of SeF_6, 0.9 mmol of SeF_5OF, and 1.0 mmol of $SeF_4(OF)_2$. The reaction was efficient for preparing about 1 mmol of $SeF_4(OF)_2$. *Caution!* When larger amounts of reactants were used, the reaction sometimes was mildly explosive and produced a high yield of SeF_6.

The compound was analyzed by allowing a 0.2211-g sample to react with excess sodium hydroxide solution in a closed glass flask. After standing about 12 hr the oxygen produced in the flask was determined by measuring the loss in weight upon pumping away the noncondensable gas while the vessel was held at −183°. The amount of hydroxide ion consumed by the reaction was determined by titrating the remaining base with 0.1 *N* HCl using bromothymol blue as an indicator. Fluoride ion was then determined by titrating with 0.2 *N* $La(NO_3)_3$ at pH 5 using an Orion fluoride-sensitive electrode. Selenium was determined gravimetrically as the element after reduction by hydroxylamine hydrochloride. *Anal.* Calcd for $SeF_4(OF)_2$: Se, 35.2; F, 50.7; OH^- consumed, 8.0 equiv/mol; O_2 liberated, 1.00 mol/mol. Found: Se, 33.5; F, 52.2; OH^- consumed, 8.09 equiv/mol; O_2 liberated, 0.97 mol/mol.

The amounts of base consumed and of oxygen produced on hydrolysis were calculated assuming that the reaction proceeded according to the equation $SeF_4(OF)_2 + 8OH^- \rightarrow SeO_4^{2-} + 4H_2O + 6F^- + O_2(g)$.

Physical Properties

Molecular Weight.—The molecular weight of the compound was determined by its vapor density. Values found were 224 and 226 (theory, 225).

Vapor Pressure and Boiling Point.—The temperature dependence of the vapor pressure, as determined by the method described by Kellogg and Cady,[4] over the range 241–286°K is given by the equation $\log P_{mm} = -(1386/T) + 7.726$, where T is the temperature in degrees Kelvin. This equation corresponds to a boiling point of 12.9°. Assuming ideal gas behavior and using the Clausius–Clapeyron equation, the latent heat of vaporization was calculated to be 6340 cal/mol, which corresponds to a Trouton constant of 22.2 cal deg^{-1} mol^{-1}.

Infrared Spectrum.—The infrared spectrum was recorded by a Beckman IR-10 spectrophotometer using a glass cell with silver chloride windows. The spectrum shown in Figure 1 has absorptions at 917 (w), 743 (s), 664 (m), and 430 cm^{-1} (s). The absorption at 917 cm^{-1} may be due to O–F stretch.[5-7] Strong absorptions occur for SeF_6 at 780 and 430 cm^{-1} and for SeF_5OF at 750 and 422 cm^{-1}.

Nuclear Magnetic Resonance Spectrum.—The nmr spectrum was obtained using a Varian Associates Model V-4311 nuclear magnetic resonance spectrometer with a 56.4-Mc oscillator. The spectrum consisted of a triplet at −47.0 ppm relative to $CFCl_3$, which was due to the four fluorine atoms in a plane around the selenium atom, and a quintuplet at −179.0 ppm relative to $CFCl_3$, which was due to the two fluorine atoms bonded to the oxygen atoms *trans* to one another. On either side of the quintuplet was a satellite about equally spaced from the center of the absorption. The relative areas of the two resonances was 2.1:1, which is close to that expected for the compound $SeF_4(OF)_2$, so it is felt that these satellites were due to the splitting of the fluorine atoms bonded to oxygen by the ^{77}Se. This spectrum shows that the two fluorine atoms of the OF groups occupy *trans* positions in the molecule.

The spin–spin coupling constant between the two sets of nonequivalent fluorine atoms was 26.8 Hz. The spin–spin coupling constant between the ^{77}Se and the four fluorine atoms in the plane had a value of 1420 Hz. This is close to ^{77}Se–F coupling constants for other compounds.[1]

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Kinetics of the *cis*-Dichlorodiammineplatinum(II)–Diethylenetriamine Reaction

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The kinetics of reactions in which the tribasic amine diethylenetriamine (dien) displaces three halide ligands in $PtBr_4^{2-}$ or $PtCl_4^{2-}$ in aqueous solutions have been reported in detail.[1,2] Because the two ammine ligands in *cis*-$Pt(NH_3)_2Cl_2$ are relatively inert[3] only two of the three nucleophilic centers in the amine would be expected to become bound to a particular platinum atom as the result of a substitution reaction. Such a product would resemble bidentate intermediates proposed for the tetrahalide substitution reactions.[1,2] Watt and Cude[4] have demonstrated that polymeric species containing platinum atoms bridged by dien groups can be obtained by the reaction of the amine with concentrated acidic solutions of $PtCl_4^{2-}$. The described *cis*-$Pt(NH_3)_2Cl_2$ reaction provides a convenient test of the tendencies for dien complexes of platinum(II) to polymerize because any monomeric product contains an unbound nitrogen center which could react with another complex ion.

Experimental Section

cis-$Pt(NH_3)_2Cl_2$ was prepared by the method of Lebedinskii

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