In our case the activation parameters ($\Delta H^* = 154$ kJ mol^{-1}, $\Delta S^* = 198$ J K^{-1} mol^{-1}) indicate that the driving force of the elimination step is the favorable entropic variation related to the removal of the large carboranyl ligand rather than the incipient formation of a H–C bond in the transition state.

The reductive elimination of H-carb from the complex **1** shows another example of a reductive-elimination process going through a preliminary ligand dissociation mechanism and can be compared with the similar behavior found in the reductive elimination of ethane from *fac*-$PtI(CH_3)_3L_2$ (L = PR_3, AsR_3),[5] $Au(CH_3)_3L$ (L = PR_3),[14] and *cis*-$Pd(CH_3)_2L_2$ (L = $PMePh_2$, PPh_3).[15]

The major novelty of this study consists (i) in the quantitative determination of all the kinetic and thermodynamic parameters and (ii) in the clear identification of an Ir^I three-coordinate complex as the primary reaction product (at least at low [PPh_3], where pathway 3 is predominant). For the principle of microscopic reversibility the reverse reaction of oxidative addition should also proceed via attack on the same coordinatively unsaturated intermediate, whereas direct attack on the squre Ir^I complex is generally reported.[16]

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Registry No. **1**, 74315-34-7; **2**, 15318-31-7; **3**, 88295-37-8; Rh(acac)$(C_2H_4)_2$, 12082-47-2.

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Novel Fluorosulfate Derivatives of Germanium(IV) and Tin(IV)

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The synthesis of fluorosulfate derivatives of germanium, $GeF_2(SO_3F)_2$, $(ClO_2)_2[Ge(SO_3F)_6]$, and $Cs_2[Ge(SO_3F)_6]$, by metal oxidation in a $HSO_3F/S_2O_6F_2$ mixture is described. In the tin system a new fluorosulfate of the composition $M[Sn(SO_3F)_5]$ ($M = K^+$ or Cs^+) is obtained. A polynuclear anionic structure is suggested with hexacoordination around tin. Structural characterizations are based on Raman, infrared, and ^{119}Sn Mössbauer spectra. Solutions in HSO_3F are studied by conductometry and NMR (^{19}F and ^{119}Sn). $K[Sn(SO_3F)_5]$ is found to be very soluble in HSO_3F and to behave as a weak acid.

Introduction

A number of simple tin(IV) fluorosulfates have been known for some time; however, the corresponding germanium compounds seem to be unknown. The tin(IV) fluorosulfates include tetrakis(fluorosulfato)tin(IV), $Sn(SO_3F)_4$,[1] difluorobis(fluorosulfato)tin(IV), $SnF_2(SO_3F)_2$,[2] and the hexakis(fluorosulfato)stannate(IV) ion $[Sn(SO_3F)_6]^{2-}$.[3] The principal preparative routes to these compounds have been the reactions of bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[4] with chloro derivatives of tin(IV). These routes are rather time consuming even though the initial reaction is rather vigorous and occasionally will proceed explosively.

Structural proposals for these compounds are based on ^{119}Sn Mössbauer and vibrational spectra, with hexacoordination for tin, common to all three, achieved by bidentate bridging fluorosulfate groups for $Sn(SO_3F)_4$ and $SnF_2(SO_3F)_2$. These proposals are supported by the known crystal structure of $(CH_3)_2Sn(SO_3F)_2$[5] and trends in the isomer shifts and quadrupole splitting data for these and other tin(IV) fluorosulfato derivatives.[6]

Our renewed interest in these compounds centers around four aspects: (i) Metal oxidation by $S_2O_6F_2$ with HSO_3F as solvent is a simple and fast route to metal fluorosulfates and fluorosulfato anions.[7] This method should afford the known compounds more efficiently and safely and may be extendable to the synthesis of germanium compounds as well. (ii) In situ generation of dissolved $Sn(SO_3F)_4$ and hopefully $Ge(SO_3F)_4$ may give HSO_3F-based superacid systems in analogy to $Au(SO_3F)_3/HSO_3F$ systems studied by us previously.[7] (iii) Synthesis of salts containing the $[Ge(SO_3F)_6]^{2-}$ anion is both a necessary prerequisite for meaningful superacidity studies on this system and a preparative challenge in view of the rather small covalent radius of germanium. (iv) We have recently synthesized a number of complexes with the previously unknown $[M(SO_3F)_5]^-$ ion, where M = Ru and Pt.[8,9] A tin(IV) analogue should be obtained and would provide a better insight into the structure through the use of ^{119}Sn Mössbauer and NMR spectroscopy.

Experimental Section

Chemicals. Commercially available chemicals of analytical or reagent grades were generally used without purification. Technical grade HSO_3F (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously. Germanium powder (325 mesh, 99.97% pure) was obtained from Ventron Corp. Tin powder (20 mesh, 99.97% pure) was supplied by BDH.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[10] chlorine dioxide, ClO_2,[11] chloryl fluorosulfate, ClO_2SO_3F,[12] and potassium fluorosulfate, KSO_3F.[13]

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Instrumentation. Raman spectra were obtained on a Spex Ramalog 5 spectrometer equipped with an argon ion laser (Spectra Physics Model 164) operating at 514.5 nm. Infrared spectra were obtained on a Perkin-Elmer 457 or 598 grating spectrophotometer. Silver chloride and bromide were used as window materials. Due to the reactivity of the samples, no mulling agents could be used and spectra were obtained on thin films. ^{19}F NMR spectra were obtained on a XL-100 spectrometer (Varian Associates). ^{19}F chemical shifts are reported with respect to $CFCl_3$ and with shifts to lower fields considered positive.

^{119}Sn FT NMR spectra were obtained on a Bruker Spectrospin 80 instrument, operated at 29.88 MHz. The samples were contained in 10-mm-o.d. NMR tubes, and the spectrometer was locked to external acetone-d_6. The Mössbauer spectrometer has been described before.[3,6]

Electrical conductance measurements were carried out with a Wayne-Kerr universal bridge, Type B221. The measuring temperature of 25.00 ± 0.01 °C was maintained in an oil bath equipped with a Sargent Thermonitor Model ST temperature-control unit. The conductivity cell, similar in design to the one described by Barr et al.,[13] was scaled down in size to allow measurements on small volumes (~20 mL). The cell constant was determined by the method of Lind et al.[14] and checked before and after each run.

All reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled by using vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. Dri Lab, Model No. HE-43-2, filled with purified dry nitrogen and equipped with a Dri-Train circulating unit, Model No. HE-93-B.

All reactions were followed by weight. Vacuum filtration of moisture-sensitive material was performed in an apparatus described by Shriver.[15] Chemical analysis was carried out by Analytische Laboratorien, Gummersbach, West Germany.

Synthetic Reactions. (a) $Sn(SO_3F)_4$. In a typical reaction 95.7 mg (0.81 mmol) of tin powder was allowed to react with a mixture of ~5 mL of $S_2O_6F_2$ and ~10 mL of HSO_3F at room temperature. A vigorous reaction ensued immediately, and after 12 h all metal had been consumed and a white precipitate had formed. Removal of all volatiles yielded 418.9 mg (0.81 mmol) of a white, moisture-sensitive solid, identified by its infrared, Raman, and ^{119}Sn Mösbauer spectra as $Sn(SO_3F)_4$. Mp: +196 °C dec (lit.[1] mp 216 °C dec).

(b) $Cs[Sn(SO_3F)_5]$. In a manner similar to that described above, tin metal granules (566 mg, 4.77 mmol) were allowed to react with a mixture of ~5 mL of $S_2O_6F_2$ and ~10 mL of HSO_3F in the presence of $CsSO_3F$, formed from the solvolysis of CsCl (802 mg, 14.76 mmol). After removal of all volatiles in vacuo at 25 °C, a white, crystalline product was obtained that analyzed as $Cs[Sn(SO_3F)_5]$ (3.492 g, 4.68 mmol). $Cs[Sn(SO_3F)_5]$ is soluble in HSO_3F. Mp: +210 °C dec. Anal. Calcd for $CsSnS_5O_{15}F_5$: S, 21.47, F, 12.72. Found: S, 21.11; F, 12.39.

$K[Sn(SO_3F)_5]$ is obtained in an identical manner. If a 2:1 molar ratio of CsCl (or KCl) to tin is used, $Cs_2[Sn(SO_3F)_6]$ (or $K_2[Sn(SO_3F)_6]$) is formed. Both are identified by their vibrational and ^{119}Sn Mössbauer spectra.

(c) $GeF_2(SO_3F)_2$. With use of a $HSO_3F/S_2O_6F_2$ mixture similar to the one described above, 440 mg (6.06 mmol) of germanium powder was allowed to react at 50 °C for 3 days, by which time all germanium had been consumed and a white precipitate had formed. In addition, a white sublimate was noted in the colder parts of the reactor. The precipitate was isolated by vacuum filtration in a closed system and subsequently washed with $S_2O_6F_2$. After vacuum drying, a white crystalline solid resulted. The yields were generally between 75 and 80%. Mp: +146 °C dec. Anal. Calcd for $GeS_2O_6F_4$: Ge, 23.52; S, 20.77; F, 24.62. Found: Ge, 23.21; S, 20.67; F, 24.51.

(d) $Cs_2[Ge(SO_3F)_6]$. In a typical reaction 1165.2 mg (6.92 mmol) of CsCl was solvolyzed in an excess of HSO_3F. The HCl evolved was removed in vacuo, and 251 mg (3.46 mmol) of germanium powder and about 5 mL of $S_2O_6F_2$ were added to the reaction vial. The mixture was allowed to react at +50 °C for 2 days, by which time all germanium had dissolved and a clear, pale yellow solution had formed. Addition of more $S_2O_6F_2$ caused the immediate formation of a white precipitate. In order to obtain crystals, this precipitate was redissolved by the careful addition of just enough HSO_3F to give rise to a clear solution. Very slow evaporation of solvent under a dynamic vacuum resulted in the crystallization of transparent, colorless crystals, which were isolated by filtration, washed with $S_2O_6F_2$, and dried in vacuo. The very hygroscopic solid melted at +242 °C. Anal. Calcd for $Cs_2GeS_6O_{18}F_6$: Ge, 7.78; Cs, 28.49; S, 20.62; F, 12.22. Found: Ge, 7.94; Cs, 28.47; S, 20.79; F, 12.35.

(e) $(ClO_2)_2[Ge(SO_3F)_6]$. A mixture of ClO_2SO_3F (~1 mL) and $S_2O_6F_2$ (~4 mL) was distilled into a reactor containing germanium metal powder (130 mg, 1.79 mmol). An exothermic reaction occurred at room temperature, and the metal dissolved into the deep red ClO_2SO_3F layer. After the reaction mixture was kept at ~50 °C for 1 day to ensure a complete reaction, the excess liquid reactants were removed in vacuo at ~80 °C over a period of 12 h. A yellow solid residue remaining in the colder parts of the reactor analyzed as $(ClO_2)_2[Ge(SO_3F)_6]$ (126 mg, 0.16 mmol). $(ClO_2)_2[Ge(SO_3F)_6]$ is a light yellow, hygroscopic solid. It is sublimable in vacuo at room temperature but melts at ~145 °C dec under an atmosphere of nitrogen. Anal. Calcd for $Cl_2GeS_6O_{22}F_6$: Ge, 9.05; F, 14.22. Found: Ge, 8.75; F, 14.22.

Results and Discussion

Synthesis. Not unexpectedly, the oxidation of tin metal by $S_2O_6F_2$ in the presence of HSO_3F proceeded quickly, smoothly, and safely at room temperature, to give quantitatively the previously known $Sn(SO_3F)_4$[1] and $M_2[Sn(SO_3F)_6]$,[3] with M = K or Cs.

Our expectations to obtain acidic solutions of $Sn(SO_3F)_4$ in HSO_3F were not realized. The polymeric $Sn(SO_3F)_4$ formed immediately, even when a large excess of acid was present. Conductivity measurements indicated some very limited solubility and some electrolytic dissociation, which however was too low for meaningful acidity studies in this system. Interestingly, $Sn(SO_3F)_4$ prepared in this study had a decomposition point of 196 °C, 20 °C lower than the literature value. It is felt that this discrepancy, which does not extend to either vibrational or Mössbauer spectra, is due to a different degree of polymerization, caused by the difference in the synthetic routes and, in particular, in the reaction temperatures, rather than the presence of impurities. Melting points found for the $M_2[Sn(SO_3F)_6]$ salts on the other hand agree extremely well with the reported values.

Salts of the overall composition $M[Sn(SO_3F)_5]$, with M = K or Cs, are readily obtained as well, according to the overall reaction

$$MCl + Sn + HSO_3F + 2S_2O_6F_2 \xrightarrow{HSO_3F} M[Sn(SO_3F)_5] + HCl \quad (1)$$

when equimolar amounts of tin and MCl are allowed to react. Both salts are very soluble in fluorosulfuric acid, which argues against their formulation as a mixture of $Sn(SO_3F)_4$ and $M_2[Sn(SO_3F)_6]$.

Attempts to obtain a mixed-valency tin fluorosulfate, analogous to $Sn^{II}Sn^{IV}(SO_3CF_3)_6$,[15] by metathesis according to

$$Sn(SO_3F)_2 + Cs_2[Sn(SO_3F)_6] \xrightarrow{HSO_3F} Sn^{II}Sn^{IV}(SO_3F)_6 + 2CsSO_3F \quad (2)$$

were unsuccessful. On mixinng, a clear solution was obtained. Removal of all volatiles yielded a solid material. The ^{119}Sn Mössbauer and vibrational spectra were composites of those of the starting materials.

When tin is replaced by germanium, the reactions generally proceed somewhat more slowly. Reaction temperatures of +50 °C and longer reaction times are needed before all germanium is consumed. The resulting product however is not the anticipated germanium tetrakis(fluorosulfate) but rather $GeF_2(SO_3F)_2$. It seems that partial decomposition of the SO_3F- groups occurs with SO_3 elimination.

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There are a number of pertinent precedents for such decomposition of main-group fluorosulfates: $SbF_3(SO_3F)_2$ decomposes at 65 °C into SO_3 and $SbF_4(SO_3F)$;[16] $PO(SO_3F)_3$, formed in the reaction of $POBr_3$ with $S_2O_6F_2$, decomposes at 100 °C to give SO_3, POF_3, POF_2SO_3F, and $POF(SO_3F)_2$;[17] and $I(SO_3F)_3$ disproportionates at 80–90 °C in vacuo to produce ISO_3F and volatile SO_3 and $IF_3(SO_3F)_2$.[18]

In all these instances relatively moderate temperatures are sufficient to cause decomposition. The isolation of analytically pure $GeF_2(SO_3F)_2$ is possible, because its low solubility in HSO_3F allows isolation by filtration. It is peculiar to this isolation method that SO_3 and other possible germanium-containing byproducts remain undetected, since the yield of 75–80% suggests the formation of GeF_4 or other germanium fluoride fluorosulfates in small quantities. The lack of solubility of $GeF_2(SO_3F)_2$ in HSO_3F precludes any solution studies on this compound aimed at the possibility of detecting a germanium-based superacid system. Interestingly, in the presence of 2 mol of $CsSO_3F$/mol of germanium, the elimination of SO_3 can be avoided. After all germanium is consumed, a pale yellow solution is formed. Slow removal of the solvent resulted eventually in the precipitation of transparent crystals, which were isolated by vacuum filtration and identified as analytically pure $Cs_2[Ge(SO_3F)_6]$. It appears that $S_2O_6F_2$ reduces the solubility of this salt in the solvent mixture. Attempts to use solvent evaporation rather than filtration resulted in partially decomposed products with $CsSO_3F$ detected by infrared spectra.

The melting point of 242 °C observed for $Cs_2[Ge(SO_3F)_6]$ is surprisingly high, considering our inability to isolate $Ge(SO_3F)_4$, but for $Cs_2[Sn(SO_3F)_6]$ a similarly high melting range of 249–253 °C was reported.[3]

Another compound with the $[Ge(SO_3F)_6]^{2-}$ ion is isolated when the oxidation of Ge by $S_2O_6F_2$ is carried out in the presence of ClO_2SO_3F as reaction medium, which also provides the counterion ClO_2^+. Isolation by evaporation in vacuo of all volatiles at ~80 °C afforded yellow, hygroscopic $(ClO_2)_2[Ge(SO_3F)_6]$ in a very low yield. Substantial loss of product seems to occur during the removal of excess reagent at 80 °C. In spite of this, isolation by removal of volatiles in vacuo appears to be safer than filtration of such a strongly oxidizing viscous mixture. The resultling yellow $(ClO_2)_2[Ge(SO_3F)_6]$ decomposes at ~145 °C, exhibiting a thermal stability similar to that reported for $(ClO_2)_2[Sn(SO_3F)_6]$.[3]

The results on the germanium oxidation presented here are somewhat puzzling. On one hand, $Ge(SO_3F)_4$ is not tractable and $GeF_2(SO_3F)_2$ forms instead. On the other hand, $[Ge(SO_3F)_6]^{2-}$ not only exists but shows, in form of the cesium salt, high thermal stability. Hence, the argument that SO_3 elimination is a consequence of steric crowding around germanium becomes untenable. It seems rather that reaction conditions as well as solubilities influence the course of the reactions. In pure HSO_3F, $GeF_2(SO_3F)_2$ precipitates from solution, due to its polymeric nature, and is hence removed from dissociation equilibria. With sufficient SO_3F^- present, $[Ge(SO_3F)_6]^{2-}$ forms instead and saltlike $Cs_2[Ge(SO_3F)_6]$ is precipitated preferentially from solution in an ionizing solvent by the addition of the nonionizing solvent $S_2O_6F_2$.

This argument implies a strong structural similarity between the tin and germanium systems, which is supported by their vibrational spectra, as discussed below.

It should also be mentioned that all attempts to utilize the synthetic route to $Cs[Sn(SO_3F)_5]$ in the germanium system were unsuccessful. Only inhomogeneous mixtures were obtained, and the observed weight changes suggest very extensive decomposition to volatile materials.

Table I. Vibrational Frequencies for $GeF_2(SO_3F)_2$ and $SnF_2(SO_3F)_2$[a]

$GeF_2(SO_3F)_2$				$SnF_2(SO_3F)_2$[b]		
IR ν, cm^{-1}	int	Ra $\Delta\nu$, cm^{-1}	int	IR ν, cm^{-1}	int	assignt
1402	vs	1426	m	1420	m, sh	$\nu(SO_3)$
				1405	vs, b	
				1115	vs, b	$\nu(SO_3)$
1109	vs, sh	1095	m	1103	s, sh	
1058	vs, b	1064	m	1070	s, b	$\nu(SO_3)$
		1055	w, sh			
895	s, sh					$\nu(SF)$
880	vs	880	vs	855	vs	
870	s, sh					$\nu(Ge{-}F)_{asym}$
770	vs					
				691	s	$\nu(Sn{-}F)$
668	s, sh					SO_3 bend[c]
662	s	656	w, sh	628	ms	
		648	ms			$\nu(Ge{-}F)_{sym}$
580	s	576	m	590	s	SO_3 bend
560	s	560	w	548	vs	SO_3 bend
500	ms	490	m			$\nu(Ge{-}OSO_2F)$
424	m	437	m	430	m, s	SO_3 rock
				350	m	$\nu(Sn{-}OSO_2F)$
		280	w			

[a] Abbreviations: IR = infrared, Ra = Raman, int = intensity, v = very, s = strong, m = medium, w = weak, b = broad, sh = shoulder, asym = asymmetric, sym = symmetric. [b] Reference 2. [c] These bands are thought to have M–O skeletal vibrations mixed in.

It can be concluded that both tin and germanium can be oxidized by bis(fluorosulfuryl) peroxide to the +4 oxidation state. The presence of HSO_3F in these reactions results in low reaction temperatures and shorter reaction times. This was convincingly illustrated by the reaction of germanium powder with $S_2O_6F_2$ in the absence of HSO_3F. In order to oxidize all Ge, a reaction temperature of 150 °C had to be maintained for about 7 days. Product isolation by evaporation of volatiles gave $GeF_2(SO_3F)_2$ in very poor yield, which makes this route unattractive.

Also, a possible complication may be briefly mentioned. Oxidation of tin with rather small amounts of $S_2O_6F_2$ in HSO_3F as reaction medium is often accompanied by a blue to green coloration of the reaction mixture. This problem is avoided by using an excess (~10 times the required amount) of $S_2O_6F_2$. In analogy to observations made by others when P_4, arsenic, or antimony is reacted with $S_2O_6F_2/HSO_3F$[19]—the last in vast excess—we suspect that the metal reduces the solvent eventually to colored polysulfur cations or free radicals.[20]

Vibrational and Mössbauer Spectra. For the compounds discussed here, infrared and Raman spectra represent the principal source of structural information. This is particularly true for the germanium derivatives, while for the tin fluorosulfates additional information is available from the ^{119}Sn Mössbauer spectra. It is fortunate that for all three new germanium compounds, $GeF_2(SO_3F)_2$, $Cs_2[Ge(SO_3F)_6]$, and $(ClO_2)_2[Ge(SO_3F)_6]$, the corresponding tin analogues are known[2,3] and their vibrational spectra should allow structural conclusions based on spectral comparison.

The strong structural similarity between $SnF_2(SO_3F)_2$ and $GeF_2(SO_3F)_2$ is apparent from the vibrational data compiled in Table I. The Raman spectrum of $GeF_2(SO_3F)_2$ is of relatively poor quality, due to strong fluorescence causing a sloping base line. This results in rather low band intensities.

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Table II. Vibrational Frequencies for $Cs_2[Ge(SO_3F)_6]$, $(ClO_2)_2[Ge(SO_3F)_6]$, and $Cs_2[Sn(SO_3F)_6]$

$Cs_2[Ge(SO_3F)_6]$				$(ClO_2)_2[Ge(SO_3F)_6]^a$				$Cs_2[Sn(SO_3F)_6]$		
Ra $\Delta\nu$, cm^{-1}	int	IR ν, cm^{-1}	int	Ra $\Delta\nu$, cm^{-1}	int	IR ν, cm^{-1}	int	Ra $\Delta\nu$, cm^{-1}	int	approx description
1420	ms, sh			1414	w			1407	m	$\nu(SO_2)_{asym}$
1408	s	1400	vs	1390	m	1385	vs	1399	m	
				1380	m					
1275	vs	1266	w	1272	ms			1270	s	$\nu(SO_2)_{sym}$
1220	mw	1218	vs	1215	s	1200	vs, b	1218	w	
				1205	s					
1098	s			1098	m			1091	s	
1052	vw									
		1010	vs			1020	vs, b			
990	mw			1001	w			995	sh	$\nu(FO_2SO-)$
				985	vw					
965	w, sh			965	w					
830	s	815	vs	847	w	820	vs, b	828	m	$\nu(SF)$
810	ms, sh	800	m, sh	821	w			811	m	
635	s	645	m	631	m	640	s	625	s	MO skel vib + SO_2 bend
585	s	585	m	591	w	580	ms	578	ms	SO_2 sym bend
560	ms	555	m	567	w	555	ms	560	ms	SO_2 asym bend
				555	w					
				461	w					
440	ms			436	m	432	w	431	m	MO skel vib
412	m, sh							418, 407	w	SO_3F rock
278	vs			270	s			345	w	MO skel vib
								260	m	
248	ms			255	m					def and lattice vib
205	m									
170	w									
108	s									

[a] Fundamentals due to ClO_2^+: Ra 1307, 1295 (ν_3), 1063 (ν_1), 526 (ν_2); IR 1305, 1295 (ν_3), 520 (ν_2).

The observed band positions for both compounds agree very well, where the bands are due to the internal SO_3F- vibrations. This indicates a strong structural similarity of both compounds. The most noteworthy features are found in the SO_3- and SF–stretching range, with three main bands in the SO_3-stretching region at about 1400, 1100, and 1060 cm^{-1} and $\nu(SF)$ at 880 cm^{-1}, indicative of a loss of C_{3v} symmetry for the fluorosulfate group and a bidentate configuration with bonding through oxygen. A bridging function of this bidentate group is more consistent with the physical data of $GeF_2(SO_3F)_2$—lack of volatility and solubility in HSO_3F—than a chelating function, which would be rather unprecedented for the SO_3F- group. The resulting polymer, most likely sheetlike as found in $(CH_3)_2Sn(SO_3F)_2$[5] rather than chainlike, seems then to have a linear or near-linear F–Ge–F configuration, completing a six-coordinate environment with local D_{4h} symmetry for germanium. Both the high local symmetry and the linear F–Ge–F configuration cause mutual exclusion of the two GeF_2 stretches. The asymmetric stretch at 770 cm^{-1} seems only IR active while the symmetric stretch at 648 cm^{-1} seems only Raman active. The same feature had been found for $SnF_2(SO_3F)_2$[2] with the corresponding bands at 691 and 612 cm^{-1}, respectively. Similar band positions are found for stretching vibrations of other Ge–F compounds: in GeF_4, $\nu_1(A_1)$ is found at 738 cm^{-1} and $\nu_3(F_2)$ at 800 cm^{-1},[21] and in GeF_6^{2-},[22] $\nu_1(A_{1g})$ is found at 627 cm^{-1} and $\nu_3(F_{1u})$ at 598 cm^{-1}. The small discrepancies in band positions reflect differences in molecular symmetry and charge.

Bands found at 660 and 550 cm^{-1} can be attributed at least in part to Ge–O skeletal vibrations with the corresponding Sn–O bands somewhat lower, reflecting the difference in masses. The structural similarity extends also to the hexakis(fluorosulfato)germanates and -stannates, as seen in Table II. The Raman spectrum of $Cs_2[Ge(SO_3F)_6]$ is depicted in Figure 1. The observed band spacing with groups of bands at ~1420, ~1260, and ~1000 cm^{-1} and $\nu(SF)$ at 830 cm^{-1} is characteristic for a monodentate $-OSO_2F$ group in an anionic complex. The band proliferation, perhaps slightly more pronounced for $(ClO_2)_2[Ge(SO_3F)_6]$, is again observed and seemingly caused by vibrational interaction between individual fluorosulfate groups, with the nonspherical ClO_2^+ causing additional band splitting. Strong to medium strong bands at about 640, 430, and 270 cm^{-1} are also a common feature of these anions, and some slight frequency dependence on the central metal atom suggests contributions from skeletal vibrations. Practically the same spectral features have previously been noted also for $[M(SO_3F)_6]^{2-}$ complexes where M = Pd,[23] Pt,[24] or Ir,[25] which leaves little doubt in regard to the identity of the $[Ge(SO_3F)_6]^{2-}$ ion in these complexes. A partial decomposition with SO_3 elimination is rather unlikely, because bands assignable to Ge–F stretching vibrations in the region of 800–650 cm^{-1} are not seen.

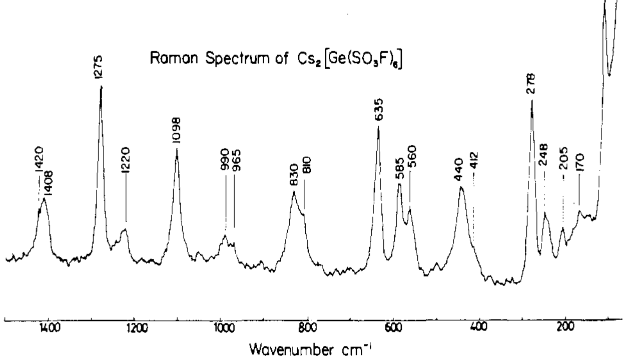

Figure 1.

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Table III. Vibrational Frequencies for Cs[$Sn(SO_3F)_5$], $Sn(SO_3F)_4$, and K_2[$Sn(SO_3F)_6$][a]

Cs[$Sn(SO_3F)_5$]				K_2[Sn-($SO_3F)_6$][a]		$Sn(SO_3F)_4$[b]	
IR ν, cm^{-1}	int	Ra Δν, cm^{-1}	int	Ra Δν, cm^{-1}	int	Ra Δν, cm^{-1}	int
		1420	m, sh			1431	m, sh
1399	vs, b	1415	ms			1425	s
		1403	m, sh	1407	m		
				1309	m		
1251	m	1260	vs	1278	s		
1212	s	1220	m	1228	m	1230	s
1186	w			1208	w		
1111	w	1118	m, sh			1120	s
1095	w	1102	ms				
		1090	w, sh	1096	s	1070	m
1080	w						
1028	m, sh	1050	mw			1047	vw
990	s	990	mw	1002	m		
						955	vw
872	w	880	mw			909	ms
851	w	843	ms	859	m	848	ms
825	m, sh	812	m	836	m		
807	s	802	m, sh	823	m		
						648	m, sh
631	m, sh	629	s	625	s	632	s
620	s						
		600	w				
580	m	580	m	582	m	589	s
555	m	550	m	560	m	560	m, b
						448	s
		430	ms	435	m	428	s
		410	m, sh	416	m	400	w
				360	m		
		292	m				
		260	s	266	w	273	vs
		212	m			248	m
		145	m, sh				

[a] Reference 3. [b] This work. The spectrum differs insignificantly from the published one ref[1] but extends down to lower frequencies.

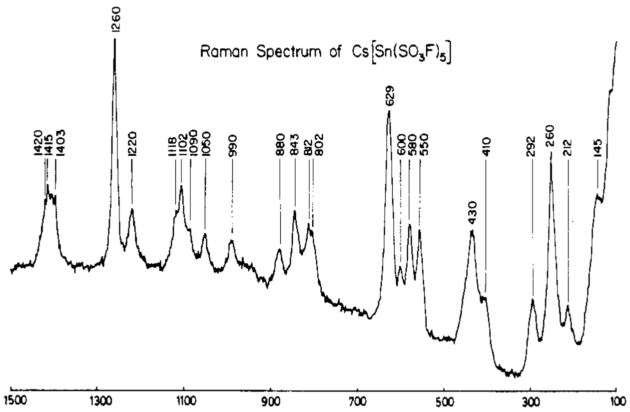

Figure 2.

The saltlike nature of $(ClO_2)_2$[$Ge(SO_3F)_6$] is also evident from the bands attributed to Cl–O vibrations. The observed positions of the three fundamentals agree well with previous findings for ClO_2^+.[26]

Table IV. ^{119}Sn Mössbauer Data of Tin(IV) Fluorosulfates at 80 K

compd	isomer shift δ,[a] mm/s	quadrupole splitting Δ, mm/s	line width Γ, mm/s	
$Sn(SO_3F)_4$[b]	−0.270	1.340	1.050	1.320
$Sn(SO_3F)_4$[c]	−0.242	1.200	1.194	1.206
Cs[$Sn(SO_3F)_5$][c]	−0.239	0.617	1.185	1.279
Cs_2[$Sn(SO_3F)_6$][d]	−0.250		1.110	
Cs_2[$Sn(SO_3F)_6$][c]	−0.261		1.118	
$SnF_2(SO_3F)_2$[e]	−0.23	1.96	1.07	1.22

[a] Relative to SnO_2. [b] References 1 and 6. [c] This work. [d] Reference 3. [e] Reference 2.

A more complex set of vibrational spectra is obtained for K[$Sn(SO_3F)_5$] and Cs[$Sn(SO_3F)_5$]. The vibrational frequencies for the latter are listed in Table III, together with Raman data for $Sn(SO_3F)_4$ and K_2[$Sn(SO_3F)_6$]. The Raman spectrum is shown in Figure 2. An assignment of individual bands is not attempted, but from the preceding discussion band spacings at ~1400, ~1200, ~1000, and ~830 cm-1 are clearly recognizable and suggest monodentate $-OSO_2F$ groups in an anionic complex. In addition, the spectra of Cs[$Sn(SO_3F)_5$] show bands at ~1120 and ~1050 cm^{-1} in the SO_3– stretching region and ν(SF) at ~870 cm^{-1}, which are attributed to a bidentate fluorosulfate, as best identified in the IR spectrum of $SnF_2(SO_3F)_2$ (Table I). A third SO_3– stretch, expected at ~1400 cm^{-1}, appears to coincide with the highest band due to the monodentate $-OSO_2F$ group.

It seems then, assuming again a bridging rather than a chelating role for the SO_3F group, that the [$Sn(SO_3F)_5$]$^-$ ion may not be monomeric but rather oligomeric. One should however concede that the frequency listing in Table III does not totally rule out the possibility of a mixture of $Sn(SO_3F)_4$ and Cs_2[$Sn(SO_3F)_6$] because of the crowding of vibrational bands in certain critical regions.

While chemical evidence such as the solubility in HSO_3F is not consistent with the presence of such a mixture, more convincing evidence comes from the ^{119}Sn Mössbauer spectrum. Table IV summarizes the spectral data for Cs[$Sn(SO_3F)_5$] as well as data obtained on the new preparations of Cs_2[$Sn(SO_3F)_6$] and $Sn(SO_3F)_4$, together with the literature data for both.

The single-line spectrum obtained for Cs[$Sn(SO_3F)_5$] can be resolved into a doublet with a rather small quadrupole splitting of 0.617 mm/s. This finding is most consistent with either a distorted octahedral environment for tin, produced by cis-fluorosulfate bridging, or a pentacoordinate structure. The latter would not be consistent with vibrational data, but a final distinction will require the sign determination of the quadrupole splitting in Cs[$SnSO_3F)_5$].

All attempts to obtain a crystal structure by X-ray diffraction have failed so far; hence, the degree of oligomerization is unknown and the empirical formulation of [$Sn(SO_3F)_5$]$^-$ is maintained.

Solution Studies in HSO_3F. The lack of any appreciable solubility of both $Sn(SO_3F)_4$ and $GeF_2(SO_3F)_2$ and our earlier report[3] on the solution behavior of K_2[$Sn(SO_3F)_6$] and $(ClO_2)_2$[$Sn(SO_3F)_6$] limit this study to two basic objectives: (a) probing the possible existence and behavior of [$Ge(SO_3F)_6$]$^{2-}$ in HSO_3F and (b) investigating the solution behavior of [$Sn(SO_3F)_5$]$^-$.

Solutions of Cs_2[$Ge(SO_3F)_6$] in HSO_3F give rise at room temperature to a sharp, single-line ^{19}F NMR resonance at 40.5 ppm relative to $CFCl_3$. In HSO_3CF_3 as the solvent, the solute resonance occurs at 40.68 ppm with the solvent resonating at −75.3 ppm. Since pure fluorosulfuric acid has a resonance at 40.56 ppm, the single line found for solutions of Cs_2[$Ge(SO_3F)_6$] in HSO_3F might well be caused by accidental overlap of both resonance lines rather than rapid exchange of SO_3F groups between solvent and solute. For K_2[$Sn(SO_3F)_6$] as solute, a single resonance at 41.37 ppm is found well separated from the solvent signal.[3]

Solutions of $(ClO_2)_2$[$Ge(SO_3F)_6$] in HSO_3F show concentration-dependent electrical conductivities, indicative of weakly

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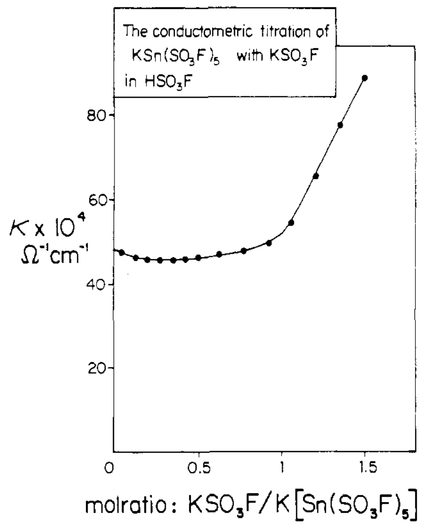

Figure 3.

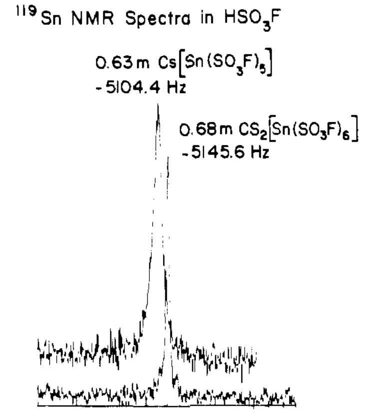

Figure 4.

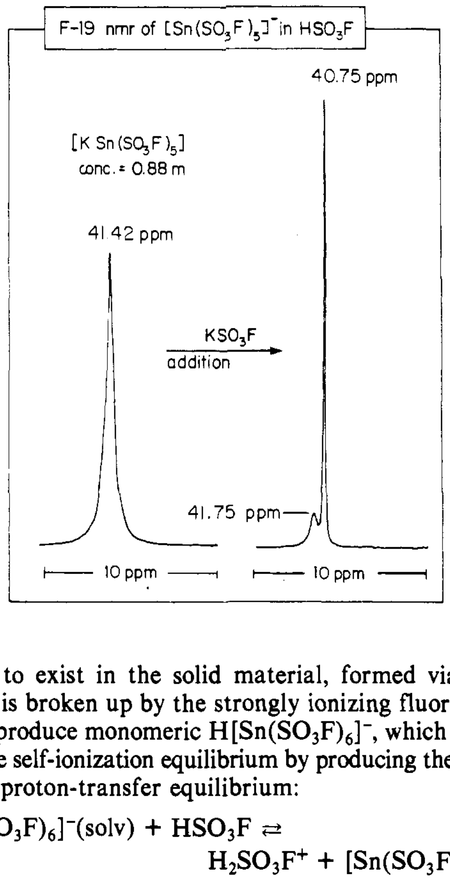

Figure 5.

basic behavior. As previously reported for $(ClO_2)_2[Sn(SO_3F)_6]$,[3] a plot of the specific conductivity, κ, against concentration up to 2.2×10^{-2} mol kg^{-1} results in a very slightly curved line, but the slope is not quite as steep as had been found for the tin analogue.[3]

The ionization behavior is best described by

$$(ClO_2)_2[M(SO_3F)_6] \rightarrow 2ClO_2^+(solv) + [M(SO_3F)_6]^{2-}(solv) \quad (3)$$

$$M = Ge, Sn$$

followed by a proton-transfer equilibrium

$$[M(SO_3F)_6]^{2-} + HSO_3F \rightarrow H[M(SO_3F)_6]^-(solv) + SO_3F^-(solv) \quad (4)$$

which seems to be more extensively shifted to the right for Sn than for Ge. This would cause a lower concentration of SO_3F^- in the latter system. Neither ^{19}F NMR nor the conductometric study provides any indication of dissociation or SO_3 elimination at room temperature. The $[Ge(SO_3F)_6]^{2-}$ species thus appears stable in HSO_3F solution.

For the second part of our conductometric solution studies in HSO_3F, the potassium salt $K[Sn(SO_3F)_5]$ was selected because it is extremely soluble in the acid. Solvent removal from its solutions does not immediately lead to precipitate formation but results in a rather viscous mass, from which HSO_3F is removed only with difficulties. In contrast, $Cs[Sn(SO_3F)_5]$ is less soluble and a concentration limit of 1.3 mol kg^{-1} is obtained at 25 °C. Furthermore, KSO_3F is commonly used as standard base and a common cation would make for a simpler system.

When specific conductance values are plotted against concentration in the range up to 4.0×10^{-2} mol kg^{-1}, a similar curve is observed with a slope slightly steeper than that reported for $K_2[Sn(SO_3F)_6]$. However, a conductometric titration, shown in Figure 3, points to a fundamental difference between both salts. $K[Sn(SO_3F)_5]$ behaves as a weak acid in HSO_3F, the first known salt to do so, with conductance due to the acidium ion $H_2SO_3F^+$ rather than the base ion SO_3F^-.

The formation of this ion is seen to proceed in the following stepwise manner: ionic dissociation

$$K[Sn(SO_3F)_5] \xrightarrow{HSO_3F} K^+(solv) + [Sn(SO_3F)_5]^-(solv) \quad (5)$$

followed by interaction with HSO_3F

$$[Sn(SO_3F)_5]^-(solv) + HSO_3F \rightarrow H[Sn(SO_3F)_6]^- \quad (6)$$

It is assumed that any polymeric or oligomeric anion that appears to exist in the solid material, formed via SO_3F-bridges, is broken up by the strongly ionizing fluorosulfuric acid, to produce monomeric $H[Sn(SO_3F)_6]^-$, which will now affect the self-ionization equilibrium by producing the acidium ion in a proton-transfer equilibrium:

$$H[Sn(SO_3F)_6]^-(solv) + HSO_3F \rightleftarrows H_2SO_3F^+ + [Sn(SO_3F)_6]^{2-} \quad (7)$$

The conductometric titration with KSO_3F shown in Figure 3 can then be described by the net equation

$$K[Sn(SO_3F)_5] + KSO_3F \xrightarrow{HSO_3F} K_2[Sn(SO_3F)_6] \quad (8)$$

The shape of the titration curve reflects the rather weak acidity of the $H[Sn(SO_3F)_6]^-$ ion. Its reaction with HSO_3F (see reaction 7) represents the second ionization step of the elusive diprotonic acid $H_2[Sn(SO_3F)_6]$, which, as stated earlier, is not present in solution in appreciable quantities on account of its tendency to polymerize to $Sn(SO_3F)_4$. Hence, a minimum is not readily apparent in the titration curve, but a definite break at a 1:1 mole ratio is noted, where now conductivity begins to be dominated by the SO_3F^- ions. Supporting evidence for the proposed solution behavior of the $[Sn(SO_3F)_5]^-$ ion comes also from NMR data. The ^{119}Sn NMR spectrum of a solution of $Cs[Sn(SO_3F)_5]$ in HSO_3F is shown in Figure 4. The single-line resonance (no ^{119}Sn–^{19}F coupling was observed in the ^{19}F NMR spectrum either) is shifted downfield by 41 Hz relative to the $[Sn(SO_3F)_6]^{2-}$ resonance. Considerable broadening is noted with a half line width of ~25 Hz com-

Inorg. Chem. **1984**, *23*, 659-667

pared to ~9 Hz for $[Sn(SO_3F)_6]^{2-}$, indicative of rapid SO_3F-group exchange between solvent and solute as postulated in eq 6.

The ^{19}F NMR spectrum, shown in Figure 5, provides complementing evidence. A concentration-dependent broad single line is observed for solutions of $K[Sn(SO_3F)_5]$ in HSO_3F. For a 0.88 mol kg^{-1} solution of $K[Sn(SO_3F)_5$, this resonance is found at 41.42 ppm with a half line width of 24 Hz. Addition of solid KSO_3F to this solution causes a splitting of this broad resonance into two sharp components, one at 41.75 ppm attributed to $[Sn(SO_3F)_6]^{2-}$ and a second at 40.75 ppm due to the solution of excess KSO_3F in fluorosulfuric acid. It appears that the ^{19}F NMR experiment allows the monitoring of the acid–base titration, described by eq 8. The exchange broadening for $[Sn(SO_3F)_5]^-$ in HSO_3F indicates a coordinatively unsaturated species, with SO_3F^- addition producing now the $[Sn(SO_3F)_6]^{2-}$ ion.

Conclusions

In view of the scarcity of germanium(IV) oxyacid derivatives, some tentative comments on both the differences and similarities of the respective tin and germanium compounds may be made. Formation of $GeF_2(SO_3F)_2$ under conditions where $Sn(SO_3F)_4$ forms quantitatively indicates a greater tendency of the Ge–SO_3F group to undergo SO_3 elimination. The resulting $GeF_2(SO_3F)_2$ shows the same structural features as the tin compound; hexacoordination is achieved by bidentate SO_3F groups with a linear F–M–F evident from the Raman and infrared spectra. The similarities in thermal stabilities, solution behavior in HSO_3F, and the vibrational spectra of the $[M(SO_3F)_6]^{2-}$ complexes are rather striking.

The solution behavior of $[Sn(SO_3F)_5]^-$ and the detected acidity in HSO_3F suggest $H_2[Sn(SO_3F)_6]$ to be a rather strong dibasic acid. However, the intrinsic tendency toward hexacoordination necessary for superacid behavior is also the driving force behind the noted polymer formation.

Acknowledgment. Financial support by the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. Professor J. R. Sams and L. Sallos are thanked for providing the ^{119}Sn Mössbauer spectra.

Registry No. $Sn(SO_3F)_4$, 88476-13-5; $Cs[Sn(SO_3F)_5]$, 88476-17-9; $K[Sn(SO_3F)_5]$, 88476-19-1; $Cs_2[Sn(SO_3F)_6]$, 37477-90-0; $K_2[Sn(SO_3F)_6]$, 37477-89-7; $GeF_2(SO_3F)_2$, 88476-15-7; $Cs_2[Ge(SO_3F)_6]$, 88476-20-4; $(ClO_2)_2[Ge(SO_3F)_6]$, 88476-22-6; Sn, 7440-31-5; $S_2O_6F_2$, 13709-32-5; Ge, 7440-56-4.

Contribution from the Chemistry Department, Faculty of Military Studies, Royal Military College,
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Steric Course of Base Hydrolysis of *cis*- and *trans*-$[Co(en)_2(N_3)X]^{n+}$ and *cis*- and *trans*-$[Co(en)_2(NCS)X]^{n+}$ (X = Br^-, Cl^-, $OS(CH_3)_2$, $OCHN(CH_3)_2$, N_3^-, O_2CH^-)

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The steric course has been determined spectrophotometrically, by using two or three independent methods, for the base hydrolysis reactions of *cis*- and *trans*-$[Co(en)_2(NCS)X]^{n+}$ and *cis*- and *trans*-$[Co(en)_2(N_3)X]^{n+}$ (X = Cl^-, Br^-, N_3^-, HCO_2^-, $(CH_3)_2SO$, $(CH_3)_2NCHO$) at 25 °C. The following *cis-/trans*-$[Co(en)_2A(OH)]^+$ product distributions (±2%) were obtained. *cis*-$[Co(en)_2(N_3)X]^{n+}$: X = Cl^-, 48% cis; Br^-, 47.5%; $OS(CH_3)_2$, 39%. *trans*-$[Co(en)_2(N_3)X]^{n+}$: X = Cl^-, 24% cis; Br^-, 26%; O_2CH^-, 23%; N_3^-, 26%; $OS(CH_3)_2$, 30.5%; $OCHN(CH_3)_2$, 26%. *trans*-$[Co(en)_2(NCS)X]^{n+}$: X = Cl^-, 82% cis; Br^-, 75%; $OS(CH_3)_2$, 72%. *trans*-$[Co(en)_2(NCS)X]^{n+}$: X = Cl^-, 70% cis; Br^-, 75%; $OS(CH_3)_2$, 72%. The study includes earlier work, widened to improve the range of leaving groups and and reexamined to improve, in some cases, the accuracy and/or precision of the steric course data. The *trans*-$[Co(en)_2(N_3)(OCHN(CH_3)_2)]^{2+}$ ion reacts in part by OH^- attack at the ligand to give *trans*-$[Co(en)_2(N_3)(O_2CH)]^+$ and $(CH_3)_2NH$, and allowance has been made for this minor (3.3%) pathway. The results are internally consistent and reveal for the first time a small but definite influence of the leaving group X on the stereochemistry of base hydrolysis products, *cis*- and *trans*-$[Co(en)_2A(OH)]^+$. For varied A and reactant geometry, there is no obvious correlation between the product distribution on X. The "rules" for stereochemical change in these classic substitution processes are examined in light of the new data. The results are best explained in terms of the S_N1CB mechanism involving short-lived, common five-coordinate intermediates. Details of this and alternative mechanisms are considered. Experiments are described that preclude the possibility of preisomerization in the $[Co(en)_2(NCS)X]^{n+}$ reactions, where the unusual stereochemical outcome is a very similar product distribution for cis and trans reactants.

Introduction

The widely accepted[1] mechanism for the base hydrolysis of octahedral amine complexes of cobalt(III) is the dissociative conjugate base process (S_N1CB[2] or DCB[3]). An integral part of the mechanism (Scheme I) has been argued[1] to be the

Scheme I

$$A_4(RNH_2)CoX^{n+} + OH^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} A_4(RNH)CoX^{(n-1)+} \xrightarrow{\text{slow}}$$

$$A_4(RNH)Co^{2+} + X^{(3-n)-} \xrightarrow[\text{fast}]{H_2O} A_4(RNH_2)CoOH_2^{\;3+}$$

formation of a reactive five-coordinate intermediate, and much evidence has been accumulated in support of their existence.[4,5]

Among the earliest work on this problem was a paper[6] indicating that the steric course of base hydrolysis of the *cis*- and *trans*-$[Co(en)_2AX]^{n+}$ ions (A, X = Cl^-, Br^-, N_3^-, NCS^-, NO_2^-, and others) was independent of the leaving group, as the mechanism requires. The data that did not show this independence were of dubious accuracy or had large experimental errors. Since then, few precise results have been forthcoming, save from some careful work[7,8] on the $\Lambda(+)$-*cis*- and *trans*-

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