ticular, the values of r(Pt–Cl) and ν(PtCl) for Y = p-CF$_3$ are respectively larger and smaller than would have been predicted for this electron-withdrawing substituent. Also, there is no correlation between ν(PtH) in *trans*-PtH(C$_6$H$_4$-p-Y)(PEt$_3$)$_2$ (measured in solution) and ν(PtCl) in *trans*-PtCl(C$_6$H$_4$-p-Y)(PEt$_3$)$_2$ (measured in the solid state). In the silyl–platinum(II) complexes *trans*-PtCl[Si(C$_6$H$_4$Y)$_3$](EMe$_2$Ph)$_2$ (E = P, As), ν(PtCl) increases as Y becomes more electron withdrawing, but the value of ν(PtCl) for Y = H is anomalously low, possibly as a result of a solid-state effect.[35]

Conclusions. Variation of meta and para substituents in the aryl groups of arylplatinum(II) complexes causes small changes in the spectroscopic parameters characterizing the metal–ligand bonds in both cis and trans positions. Many of these changes fit the DSP equation reasonably well, the correlation being uniformly better for meta than for para substituents, i.e. f(para) > f(meta) in Table III. Concepts such as the inductive and resonance transmission of electronic effects are therefore transferable from aromatic organic compounds to arylplatinum(II) complexes, in agreement with earlier work.[13–15] Anomalous features are the insensitivity of ^1J(PtH) to the nature of a para-substituted aryl group and the poor correlation with the DSP equation of ^1J(PtP) trans to a para-substituted aryl group, for which we have no satisfactory explanation.

The most unexpected regularity is the increase (decrease) of ^1J(PtP) cis to an aryl group caused by electron-donating (-withdrawing) meta and para substituents. In a recent structural comparison of *trans*-PtCl(CH$_3$)(PMePh$_2$)$_2$ and *trans*-PtCl(C$_2$F$_5$)(PMePh$_2$)$_2$, we found that the Pt–P bonds in the fluoroalkyl complex are about 0.04 Å longer than those in the methyl complex and suggested that this might be a steric lengthening caused by the considerably shorter Pt–C and Pt–Cl bonds in the fluoroalkyl complex.[36] The longer Pt–P distance in the fluoroalkyl complex is also associated with a smaller value of ^1J(PtP). The trend in the arylplatinum(II) complexes is understandably smaller in magnitude, but it operates in the same sense, and it seems more likely to be electronic in origin. An explanation based on π-back-bonding competition between aryl or fluoroalkyl groups and the phosphine ligands similar to that used to account for the trends in *cis*-PtCl$_2$(PEt$_3$)L (see above)[29] seems to us unconvincing.

Perhaps the most reasonable explanation of the cis influence in our complexes is provided by Shustorovich's perturbation approach.[22] When one ligand in a planar ML$_4$ complex is replaced by a better σ donor, the s and d contributions to the change in overlap population in the trans position are always negative and larger than the p contribution, which is always positive. In contrast, the s and d contributions to the change in overlap contribution in the cis bonds are always of opposite sign, the s being positive and the d negative. Thus, in principle, the cis influence may be of either sign and, in the present case, we must assume that the s contribution outweighs the d contribution. This assumption is not unreasonable, since trialkylphosphines have a fairly high trans influence[1] and presumably make a high demand on Pt 6s electron density.

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Supplementary Material Available: Listings of analytical data and melting points for *trans*-PtBr(C$_6$H$_4$Y)(PEt$_3$)$_2$ complexes (Table I) and analytical data, melting points, and recrystallization solvents for *trans*-PtH(C$_6$H$_4$Y)(PEt$_3$)$_2$ complexes (Table II) (3 pages). Ordering information is given on any current masthead page.

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Fluorosulfates of the Noble Metals. 5. Fluorosulfato Derivatives of Platinum(IV) and the HSO$_3$F–Pt(SO$_3$F)$_4$ Superacid System

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A simple synthetic route to pure Pt(SO$_3$F)$_4$ is described. This compound is found to be an excellent fluorosulfate ion acceptor, forming either [Pt(SO$_3$F)$_6$]$^-$ or an oligomeric anion of the composition [Pt(SO$_3$F)$_5$]$^-$. A number of complexes with the counterions Cs$^+$, ClO$_2^+$, Ba^{2+}, and Br$_3^+$ are synthesized and characterized by vibrational spectroscopy. In a solution of HSO$_3$F the novel dibasic acid H$_2$[Pt(SO$_3$F)$_6$] is formed, which undergoes the following dissociation equilibria: H$_2$[Pt(SO$_3$F)$_6$] + HSO$_3$F $\rightleftharpoons$ H[Pt(SO$_3$F)$_6$]$^-$ + H$_2$SO$_3$F$^+$ and H[Pt(SO$_3$F)$_6$]$^-$ + HSO$_3$F $\rightleftharpoons$ [Pt(SO$_3$F)$_6$]$^{2-}$ + H$_2$SO$_3$F$^+$. The system is investigated by electrical conductance measurements and ^{19}F NMR, Raman, IR, and UV–visible spectroscopy.

Introduction

The first fluorosulfate of platinum, Pt(SO$_3$F)$_4$, was reported in 1972.[1] The synthesis was accomplished by the oxidation of platinum metal using a large excess of bromine(I) fluorosulfate. To achieve complete conversion, a temperature of 95 °C and a reaction time of 3 weeks were required. In addition, reaction intermediates, formulated as Pt(SO$_3$F)$_4$·nBrSO$_3$F, with n initially 3.5, required pyrolysis in vacuo over several days, with temperatures ranging up to 110 °C. While this route seemed rather tedious and time consuming, it had suggested to us the possibility of using Pt(SO$_3$F)$_4$ as a fluorosulfate ion acceptor, and two salts containing [Pt(SO$_3$F)$_6$]$^{2-}$ were subsequently synthesized: Ag$^{\text{II}}$[Pt(SO$_3$F)$_6$][2] and Pd$^{\text{II}}$[Pt(SO$_3$F)$_6$].[3]

The main objective in the previous studies had been the characterization of the cations Ag^{2+} and Pd^{2+}, rather than of the anion. The present study is undertaken with three ob-

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jectives in mind: (a) to find a simpler alternative to the previously[1] described synthesis of $Pt(SO_3F)_4$, attempts by us to use the reported method resulting in products that were slightly paramagnetic, rather unusual in the chemistry of Pt(IV); (b) to synthesize a range of complexes, containing the $[Pt(SO_3F)_6]^{2-}$ ion, by various routes and characterize them; (c) to probe into the solution chemistry of $Pt(SO_3F)_4$ in the hope of finding a new superacid system, as has been found recently in the $Au(SO_3F)_3/HSO_3F$ system.[4] There had been a report[5] of acidic behavior, when PtF_4 was dissolved in HSO_3F; however, the limited solubility of the tetrafluoride had precluded a more detailed study.

Full characterization of $Pt(SO_3F)_4$ and the $[Pt(SO_3F)_6]^{2-}$ salts by vibrational spectroscopy was seen as a necessary prerequisite for meaningful solution studies.

Experimental Section

Chemicals. Commercially available chemicals of analytical reagent or of reagent grade were generally used without purification. Technical grade HSO_3F (Baker and Adamson) was purified by double distillation at atmospheric pressure as described previously.[10] Platinum powder, −60 mesh, 99.9% pure, was obtained from Ventron Corp.

The following compounds were synthesized according to published methods: bis(fluorosulfuryl) peroxide, $S_2O_6F_2$,[6] bromine(I) fluorosulfate, $BrSO_3F$,[7] chlorine dioxide, ClO_2,[8] chloryl fluorosulfate, ClO_2SO_3F,[9] and potassium fluorosulfate, KSO_3F.[10]

Details on our instrumentation and special techniques used to record Raman, IR, and ^{19}F NMR and FT-NMR spectra and electrical conductivities have been published previously.[4]

All reactions were performed in Pyrex reaction vials of about 40-mL capacity, fitted with Kontes Teflon stem valves. Volatile materials were handled with use of vacuum-line techniques. Solids were handled in a Vacuum Atmospheres Corp. Model No. HE-43-2 "Dri Lab", filled with purified dry nitrogen and equipped with a Model No. HE-93-B "Dri-Train" circulating unit. Magnetic measurements at room temperatures were made on solid samples by the Gouy method. Diamagnetic susceptibilities were calculated from Pascal's constants with use of tabulations in a standard reference test[12] or approximations as follows in $10^{-6} \times cm^3\ mol^{-1}$:

$$SO_3F^- = -40 \qquad Br_3^+ = 3 \times Br = -91.8 \qquad ClO_2^+ = -28.1$$

Synthetic Reaction and Analysis. Microanalysis was performed by Analytische Laboratorien, Gummersbach, West Germany.

Platinum Tetrakis(fluorosulfate), $Pt(SO_3F)_4$. In a typical reaction, platinum powder (233 mg, 1.19 mmol) was reacted with a mixture of $S_2O_6F_2/HSO_3F$ at 120 °C for 2 days. The orange solution gave, after the removal of all volatile materials, dark yellow crystals of $Pt(SO_3F)_4$ (692 mg, 1.07 mmol).

$Pt(SO_3F)_4$ is a deep yellow to light orange, crystalline, hygroscopic solid. It melts with decomposition at 220 °C and is very soluble in HSO_3F. The microanalysis of the compound had been reported previously.[1] Magnetic properties: $\chi_M = -(81 \pm 17) \times 10^{-6}\ cm^3\ mol^{-1}$; $\sum\chi_{dia} = -188 \times 10^{-6}\ cm^3\ mol^{-1}$.

Cesium Hexakis(fluorosulfato)platinate(IV), $Cs_2[Pt(SO_3F)_6]$. $CsSO_3F$, formed by the solvolysis of CsCl (302 mg, 1.80 mmol) in HSO_3F, was mixed with a stoichiometric amount of platinum metal powder (175 mg, 0.897 mmol) and reacted with $S_2O_6F_2$ (~3 mL) and HSO_3F (~5 mL). The reaction require heating at 80 °C for 3 days, after which time a light yellow solution had formed. The evacuation of all volatile materials yielded $Cs_2[Pt(SO_3F)_6]$ as a light yellow, crystalline, hygroscopic solid. It is soluble in HSO_3F and melts with decomposition at ~260 °C. Anal. Calcd for $Cs_2Pt(SO_3F)_6$: Cs, 25.19; Pt, 18.49; S, 18.23; F, 10.80. Found: Cs, 25.03; Pt, 18.39; S, 18.32; F, 10.72.

Chloryl Hexakis(fluorosulfato)platinate(IV), $(ClO_2)_2[Pt(SO_3F)_6]$. ClO_2SO_3F (~1 mL) was added to a sample of $Pt(SO_3F)_4$ (828 mg, 1.400 mmol). A portion of $Pt(SO_3F)_4$ was found to dissolve in the liquid which was heated at ~60 °C for 1 day. The removal of all volatile materials at ~70 °C gave $(ClO_2)_2[Pt(SO_3F)_6]$.

The compound can also be prepared by the reaction of platinum metal with a mixture of $S_2O_6F_2$ and ClO_2SO_3F according to

$$Pt + 2ClO_2SO_3F + 2S_2O_6F_2 \rightarrow (ClO_2)_2[Pt(SO_3F)_6]$$

at 160 °C for 2 days followed by the removal of all volatile materials at 70 °C.

$(ClO_2)_2[Pt(SO_3F)_6]$ is a light yellow, crystalline, hygroscopic solid. It is soluble in HSO_3F and melts with decomposition at ~195–200 °C. Anal. Calcd for $Cl_2O_4Pt(SO_3F)_6$: Cl, 7.67; Pt, 21.11; F, 12.33. Found: Cl, 7.60; T, 21.24; F, 12.42. Magnetic properties: $\chi_M = -(250 \pm 15) \times 10^{-6}\ cm^3\ mol^{-1}$; $\sum\chi_{dia} = -320 \times 10^{-6}\ cm^3\ mol^{-1}$.

Barium Hexakis(fluorosulfato)platinate(IV), $Ba[Pt(SO_3F)_6]$. Anhydrous $BaCl_2$ (88 mg, 0.432 mmol) was converted into the fluorosulfate by reaction with HSO_3F (~5 mL). After the removal of the HCl evolved, $S_2O_6F_2$ (~2 mL) was distilled onto the equimolar mixture of $Ba(SO_3F)_2$ and platinum-metal powder (82 mg, 0.420 mmol) in HSO_3F. After the mixture was heated at 140 °C for 3 days, all the metal had dissolved and a light yellow precipitate had formed. The removal of all volatile materials yielded $Ba[Pt(SO_3F)_6]$.

$Ba[Pt(SO_3F)_6]$ is a light yellow, hygroscopic powder. It is only sparingly soluble in HSO_3F and melts with decomposition at ~190 °C. Anal. Calcd for $BaPt(SO_3F)_6$: Ba, 14.82; Pt, 21.05, F, 12.03. Found: Ba, 14.83; Pt, 21.03; F, 12.27. Magnetic properties: $\chi_M = -(271 \pm 6) \times 10^{-6}\ cm^3\ mol^{-1}$; $\sum\chi_{dia} = -292 \times 10^{-6}\ cm^3\ mol^{-1}$.

Bis(dibromobromonium) Hexakis(fluorosulfato)platinate(IV), $(Br_3)_2[Pt(SO_3F)_6]$. Platinum-metal powder (157 mg, 0.805 mmol) was reacted with a large excess of $BrSO_3F$ (~10 mL) at 140 °C for 7 days. About 1 mL of Br_2 was added to the mixture, which was heated at ~70 °C for about 5 min. The subsequent removal of all volatile materials at room temperature yielded a compound that was analyzed as $(Br_3)_2[Pt(SO_3F)_6]$ (998 mg, 0.787 mmol).

$(Br_3)_2[Pt(SO_3F)_6]$ is a drak brown, polycrystalline, hygroscopic solid. Prolonged standing at room temperature in vacuo causes the slow evolution of Br_2, but the compound is reasonably stable under an atmosphere of nitrogen, where it decomposes at ~90 °C. Anal. Calcd for $Br_6Pt(SO_3F)_6$: Br, 37.78; Pt, 15.37; F, 8.98. Found: Br, 38.05; Pt, 15.36; F, 8.84. Magnetic properties: $\chi_M = -(440 \pm 20) \times 10^{-6}\ cm^3\ mol^{-1}$; $\sum\chi_{dia} = -454 \times 10^{-6}\ cm^3\ mol^{-1}$.

Cesium Pentakis(fluorosulfato)platinate(IV), $Cs[Pt(SO_3F)_5]$. Stoichiometric amounts of CsCl (102 mg, 0.606 mmol) and platinum-metal powder (118 mg, 0.605 mmol) were mixed in a reactor. HSO_3F (~2 mL) was added to solvolyze the CsCl and the resultant solution evacuated to remove all HSO_3F and HCl. A mixture of $S_2O_6F_2/HSO_3F$ (~4 mL) was then added and the reaction vial held at 800 °C for 3 days, after which time all the metal had dissolved and a light orange solution had formed. The removal of all volatile materials yielded a compound that was analyzed as $Cs[Pt(SO_3F)_5]$ (503 mg, 0.608 mmol).

$Cs[Pt(SO_3F)_5]$ is a light yellow, crystalline solid, soluble in HSO_3F. It melts with decomposition at ~154 °C to an orange liquid. Anal. Calcd for $CsPt(SO_3F)_5$: Cs, 16.11; Pt, 23.35; F, 11.53. Found: Cs, 15.93; Pt, 23.41; F, 11.63.

Results and Discussion

Synthetic Reactions. Platinum (tetrakisfluorosulfate), $Pt(SO_3F)_4$, like $Au(SO_3F)_3$,[4] can be prepared conveniently by the oxidation of metal powder with $S_2O_6F_2$ using HSO_3F as solvent at a temperature of 120 °C. The oxidation is complete within 2 days; the yield is quantitative. The relatively lower reactivity of platinum is reflected in higher reaction temperatures and longer reaction times. Some difficulty is encountered when the excess of HSO_3F is removed from the product. This may indicate a stronger solvent–solute interaction in the Pt system. As a consequence of the high reaction temperature some etching of the reaction vessel occurs.

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Table I. Vibration Frequencies of $Pt(SO_3F)_4$, $Au(SO_3F)_3$, and $Sn(SO_3F)_4$[c]

$Pt(SO_3F)_4$				$Au(SO_3F)_3$[a]		$Sn(SO_3F)_4$[b]		
Ra $\Delta\nu$, cm^{-1}	int	IR ν, cm^{-1}	int	IR ν, cm^{-1}	int	Ra $\Delta\nu$, cm^{-1}	int	approx assignt
1445	m	~1440	vs, b	1442	vs	1431	s	$\nu_{as}(SO_3)$
				1425	s, sh	1420	s, sh	
1230	vs	1225	vs	1240	s	1233	s	$\nu_s(SO_2)$
				1220	s, sh			
		1150	s, vb	1135	ms	1124	s	$\nu_{as}(SO_3)$
1060	w	~1070	vs, vb	1055	s	1075	s	
		~1000	vs, vb	960	s, b	986	w	
				920	s, sh	911	m	
900	s, b	~900	vs, vb	895	s, b			
~822	vw	~820	s, vb	820	s, b	845	m	$\nu(SF)$
						827	m	
				682	s			$\nu_s(MO)$ + MO–S def
		~670	s, b	670	s, sh			
640	s	~640	s, b	~650	w, sh	640	w, sh	
~615	w, sh			610	w	632	s	SO_3F def
				590	s	589	s	
		580	s	582	s			
545	w	540	m	550	s	552	m	SO_3F rock
454	m			460	m	427	s	$\nu_{as}(MO)$ + MO–S def
293	s					320	w	$\nu_s(MO)$ + SO_3F rock
268	s							

[a] Reference 4. [b] Reference 15. [c] Abbreviations: Ra = Raman, IR = infrared, int = estimated intensity, s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad, def = deformation mode, rock = rocking mode.

The resulting material is essentially diamagnetic. The discrepancy between experimental and calculated magnetic susceptibilities may be due to a very small TIP (temperature-independent paramagnetism) contribution. Similar discrepancies are also found for $Cs_2[Pt(SO_3F)_6]$ and $(ClO_2)_2[Pt(SO_3F)_6]$.

The isolation of $(Br_3)_2[Pt(SO_3F)_6]$, coupled with our inability to obtain stable adducts when $Pt(SO_3F)_4$ is dissolved in an excess of $BrSO_3F$, allows some conjecture regarding the nature of the intermediates in the Pt–$BrSO_3F$ reaction. Oxidation by $BrSO_3F$ produces Br_2 and the reaction

$$6BrSO_3F + Pt \rightarrow (Br_3)_2[Pt(SO_3F)_6] \qquad (1)$$

becomes feasible, at least on paper. In practice, some additional Br_2 needs to be added, to allow quantitative formation of $(Br_3)_2[Pt(SO_3F)_6]$. Preparation of pure $Pt(SO_3F)_4$ could now occur via decomposition of the thermally marginally stable $(Br_3)_2[Pt(SO_3F)_6]$. Interestingly, the materials so obtained have a dark brown color, whereas the Pt–$S_2O_6F_2$ oxidation leads to a deep yellow to orange solid.

The reactions leading to the other three hexakis(fluorosulfato)platinate(IV) complexes proceed in a simple, straightforward manner. There is little doubt that the general reaction

$$2MCl + Pt + 2HSO_2F + 2S_2O_6F_2 \xrightarrow[-2HCl]{HSO_3F} M_2[Pt(SO_3F)_6] \qquad (2)$$

can be extended to other 1A, 2A, and possibly 2B metal halides. In addition, the previously published complexation reactions

$$M(SO_3F)_2 + Pt(SO_3F)_4 \xrightarrow{HSO_3F} M[Pt(SO_3F)_6] \qquad M = Ag^2 \text{ or } Pd^3 \qquad (3)$$

widen the scope to transition elements as well. Furthermore, both $(ClO_2)[Pt(SO_3F)_6]$ and $(Br_3)_2[Pt(SO_3F)_6]$ provide examples for the stabilization of nonmetallic cations. A similarly wide scope of synthetic possibilities had previously been noted for $Au(SO_3F)_3$ acting as fluorosulfate ion acceptor.[4,13]

The formation of $Cs[Pt(SO_3F)_5]$ according to the overall equation

$$CsCl + Pt + HSO_3F + 2S_2O_6F_2 \xrightarrow{HSO_3F} Cs[Pt(SO_3F)_5] + HCl \qquad (4)$$

follows recent precedents. $M[Sn(SO_3F)_5]$[11] or $M[Ru(SO_3F)_5]$,[14] with M = K or Cs, are formed in an identical manner. The ^{119}Sn Mössbauer spectrum and the solution behavior of the compound in HSO_3F had indicated a genuine complex compound rather than a mere mixture.

Attempts to prepare platinum fluorosulfate derivatives with the metal in oxidation states other than +4 were unsuccessful. No further oxidation of $Pt(SO_3F)_4$ by $S_2O_6F_2$ is noted, even at temperatures well above 100 °C. While $[Pd(SO_3F)_6]^{2-}$ is readily reduced by bromine to give $[Pd(SO_3F)_4]^{2-}$, $[Pt(SO_3F)_6]^{2-}$ is found to be unreactive under similar conditions. Solvolysis reactions of $PtCl_2$ or $PtCl_4^{2-}$ in HSO_3F at 25 and at 80 °C do not seem to take place to any significant extent. Controlled oxidation of platinum powder by $S_2O_6F_2$ does not result in the formation of Pt(II) species.

While the outcome of all these attempts is disappointing, they underscore the stability of Pt(IV) fluorosulfates toward reduction as well as oxidation.

Vibrational Spectra. Vibrational spectra obtained for $Pt(SO_3F)_4$ samples are of rather poor quality. The Raman spectra suffer from a low scattering efficiency and a limited stability of the samples in the laser beam. The infrared spectra, obtained without using mulling agents, show rather broad, poorly resolved bands, particularly in the 800–1400-cm^{-1} region.

The data obtained for $Pt(SO_3F)_4$ are listed in Table I and compared to IR data for $Au(SO_3F)_3$[4] and Raman shifts for $Sn(SO_3F)_4$.[15] A certain spectral complexity, especially in the SO- and SF-stretching region (1450–800 cm^{-1}) is common to all three compounds. The occurrence of both monodentate $-OSO_2F$ groups (commonly observed band positions for the three SO_3 stretches are ~1450, ~1230, and ~1000 cm^{-1}) and bidentate groups (with frequencies generally at ~1400, ~1120, and ~1070 cm^{-1}), must be seen as the most likely

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Table II. Raman Shifts of Various $[Pt(SO_3F)_6]^{2-}$ Complexes

ClO_2^+		Cs^+		Ba^{2+}		Br_3^+		$Cs_2[Pd(SO_3F)_6]$[a]		
$\Delta\nu$, cm^{-1}	int	$\Delta\nu$, cm^{-1}	int	$\Delta\nu$, cm^{-1}	int	$\Delta\nu$, cm^{-1}	int	$\Delta\nu$, cm^{-1}	int	descripn
1406	m	1416	w, sh	1397	w	~1400	vw	1405	w	$\nu_{as}(SO_2)$
1375	m	1410	m	1386	m	~1377	w	1395	vw, sh	
1300	vw									$\nu_{as}(ClO_2^+)$
1250	vs	1250	vs	1258	vs	1229	m	1236	vs	$\nu_s(SO_2)$
1220	vw, sh									
1208	m	1219	m	1218	m	1199	w	1212	m	
1045	s									$\nu_s(ClO_2^+)$
1022	w	1043	s	1033	m	1045	w	1020	vs	$\nu_{as}(SO_2)$
1003	w	1010	m	1012	w	~1005	vw	995	ms	
852	w			857	w			835	vw	$\nu(SF)$
826	vw			838	vw			805	vw	
807	vw	~800	w, b					785	w	
631	s	634	vs	629	vs	634	w	618	ms	$\nu_s(MO) + SO_3F$ def
580	vw	579	vw	583	vw			~585	vw, sh	SO_3F def
546	vw	550	vw	549	vw			542	w	
517	w									$\delta(ClO_2^+)$
445	m	444	m	460	m	450	w	441	ms	$\nu_{as}(MO) + SO_3F$ def
				422	vw					
~410	vw, b			411	w			~400	vw	SO_3F def
						295	m			$\nu(Br_3^+)$
283	s	280	vs	283	vs	272	m	270	s	$\nu_s(MO) + SO_3F$ def

[a] Reference 3.

cause for this complexity with $\nu(SF)$ at ~900 and 820 cm^{-1}. As suggested for $Sn(SO_3F)_4$,[15] and for $Au(SO_3F)_3$,[4] a polymeric structure produced by bidentate bridging fluorosulfate groups is most consistent with the vibrational spectra for $Pt(SO_3F)_4$. Their poor quality precludes a more detailed assignment.

Unlike $Pt(SO_3F)_4$, the three ionic complexes containing the $[Pt(SO_3F)_6]^{2-}$ anion with ClO_2^+, Cs^+, and Ba^{2+} as cations were found to be excellent Raman scatterers. $(Br_3)_2[Pt(SO_3F)_6]$, however, presented a problem similar to that for the analogous Au(III) complex. As a result of its dark color and low Raman scattering efficiency, only poorly resolved Raman spectra could be obtained, even at ~80 K. The Raman frequencies of the four $[Pt(SO_3F)_6]^{2-}$ complexes are listed in Table II together with data for $Cs_2[Pd(SO_3F)_6]$ and an approximate assignment. Band positions and intensities found are rather similar to those of spectra reported for the $[Sn(SO_3F)_6]^{2-}$ anion.[16] Since vibrational data for $Pd[Pt(SO_3F)_6]$ and $Ag[Pt(SO_3F)_6]$ have been reported, a few comments regarding the hexakis(fluorosulfato)platinate(IV) spectra with nonmetallic cations should suffice.

For $(ClO_2)_2[Pt(SO_3F)_6]$, ν_{as} of ClO_2^+, found at 1298 and 1285 cm^{-1} in the IR spectrum, shows splitting caused by the isotopes ^{37}Cl and ^{35}Cl. Band positions for all fundamentals of ClO_2^+ agree well with published data.[17]

The IR spectrum of $(Br_3)_2[Pt(SO_3F)_6]$, down to ~400 cm^{-1}, shows bands due only to the $[Pt(SO_3F)_6]^{2-}$ anion. In the low-temperature Raman spectrum, all major bands due to the anion are also present, together with new features at 295, 355, and ~700 cm^{-1} (not listed in Table II). The two higher frequency bands show band spacing and intensities typical of the resonance Raman spectrum of Br_2^+. The peak at 295 cm^{-1} compares reasonably well with the value of $\nu(Br_3^+)$ found at 290 cm^{-1} in superacid solutions[18] and the band at 280 cm^{-1} in $Br_3[Au(SO_3F)_4]$, attributed to Br_3^+.[13] Bands due to Br_2^+ seems to be present in all the Raman spectra of Br_3^+-containing complexes studied by us.[13] It may either be formed as a decomposition product in the laser beam or initially be present in low concentrations, with the band intensity enormously enhanced by the resonance Raman effect. The presence of Br_2^+ could also account for the slight paramagnetism of samples of $Pt(SO_3F)_4$ prepared by the thermal decomposition of $(Br_3)_2[Pt(SO_3F)_6]$.

Both the Raman and the IR spectra of $Cs[Pt(SO_3F)_5]$ have features that can be ascribed to the presence of both monodentate and bidentate SO_3F groups. The vibrational frequencies of $Cs[Pt(SO_3F)_5]$ are listed in Table III together with those of $Cs[Sn(SO_3F)_5]$.[14]

A detailed comparison of band positions seems to argue against the possibility that the compound is simply a mixture of $Pt(SO_3F)_4$ and $Cs_2[Pt(SO_3F)_6]$. A more convincing argument has been made for the seemingly related compound $Cs[Sn(SO_3F)_5]$ based on the ^{119}Sn Mössbauer spectrum, which implies only a single environment for Sn in this complex.[11]

A spectral comparison between $Cs[Pt(SO_3F)_5]$ and its tin(IV) analogue indicates generally good agreement, with relatively few discrepancies.

Solution Studies in HSO_3F. All three species discussed previously, $Pt(SO_3F)_4$, $M[Pt(SO_3F)_5]$, and $M_2[Pt(SO_3F)_6]$, show considerable solubility in HSO_3F and are hence suitable for solution studies. Initial evidence from electronic spectra, ^{19}F NMR spectra, and Raman spectra of solutions suggests a rather similar species to be formed on dissolution of all three solutes in HSO_3F.

The electronic spectra of $Pt(SO_3F)_4$ and $Cs_2[Pt(SO_3F)_6]$ are identical with a rather broad band (half-width ~70 nm) at $\lambda_{max} = 245$ nm and $\epsilon_{max} \approx 1.5 \times 10^4$ mol^{-1} cm^{-1}. Comparison with the spectrum of $PtCl_6^{2-}$[19] ($\lambda_{max} = 262$ nm, $\epsilon_{max} = 2.45 \times 10^4$) suggests assignment as a ligand to metal charge-transfer band in an octahedrally coordinated Pt(IV) fluorosulfate species.

The Raman spectrum of $Pt(SO_3F)_4$ in HSO_3F shows only three clearly identifiable bands at 638, 455, and 276 cm^{-1}8, which are also found in the Raman spectra of solid complexes containing the $[Pt(SO_3F)_6]^{2-}$ ion. They are attributed, at least in part, to $[PtO_6]$ skeletal vibrations (see Table II).

The ^{19}F NMR spectra of $Pt(SO_3F)_4$, $Cs[Pt(SO_3F)_5]$, and $Cs_2[Pt(SO_3F)_6]$ in HSO_3F are identical. As seen in Figure 1, a strong, sharp resonance at δ 47.75 with satellite bands due

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Table III. Vibrational Frequencies of $Cs[Pt(SO_3F)_5]$ and $Cs[Sn(SO_3F)_5]$

$Cs[Pt(SO_3F)_5]$				$Cs[Sn(SO_3F)_5]^a$				
Ra		IR		Ra		IR		
$\Delta\nu$, cm^{-1}	int	ν, cm^{-1}	int	$\Delta\nu$, cm^{-1}	int	ν, cm^{-1}	int	approx assignt
1442	vw, sh			1430	vw			$\nu_s(SO_3)$ monodentate and bidentate
1412	m	1400	vs	1418	w	~1400	vs, b	
1390	vw							
1250	vw, sh							$\nu_s(SO_3)$
1240	s			1265	m	1260	m	
1225	w, sh	1210	vs	~1220	w, b	1220	vs	
						1190	s, b	$\nu_s(SO_2)$ bidentate
		1120	s	1130	w	1125	s, b	
						1112	w	
1080	vw					1080	s, b	
1058	w			1062	w			$\nu(OSO_2)$ monodentate
1050	w, sh	1040	m					
1005	m			~1002	vw			
980	w, b							
967	w, b	950	vs, b			~1000	vs, b	
930	w	920	vs, b					
						880	w	$\nu(SF)$
835	w			850	w	~830	w, sh	
817	w	800	vs, b	820	w	800	vs, b	
658	w	670	w, sh					$\nu_s(MO) + SO_3F$ def
635	s	650	m, b	630	m	625	m, b	
605	w			605	vw			SO_3F def
590	vw					595	w	
580	vw	580	m	585	w	587	m	
547	w	540	m	560	w	560	m	
510	w	515	vw, sh					
447	m	~400	w, sh	~430	w, sh	~450	vw, sh	$\nu_{as}(MO) + SO_3F$ def
410	vw							
275	s							$\nu_s(MO) + SO_3$ bend

[a] Reference 11.

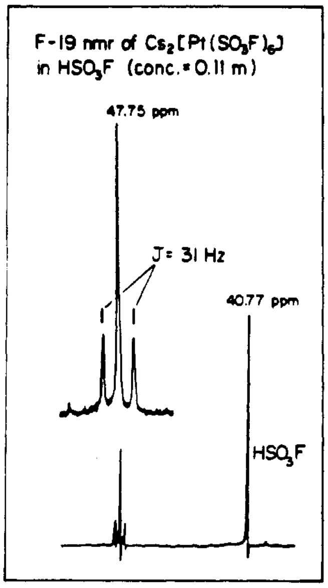

Figure 1.

to $^{195}Pt-^{19}F$ coupling is obtained with $J = 31$ Hz, substantially lower than $J(Pt-F)$ in PtF_6^{2-}, where a value of ~2000 Hz is reported.[20] A separate resonance is found for HSO_3F at δ 40.7, in excellent agreement with a δ value of 40.56 for the neat acid. This finding and the observation of a single proton signal argue against SO_3F-group exchange between solute and solvent, while proton transfer between solute and solvent still seems to occur. Unfortunately no ^{195}Pt NMR spectrum is obtainable on any of the platinum fluorosulfate derivatives in HSO_3F solution, even at concentrations up to ~1.0 mol kg^{-1}. The low sensitivity of the ^{195}Pt nucleus may be the main cause for this failure.

It appears then, that a hexakis(fluorosulfato)platinate(IV) species is formed, when $Pt(SO_3F)_4$, $Cs[Pt(SO_3F)_5]$, or $Cs_2[Pt(SO_3F)_6]$ is dissolved in fluorosulfuric acid. This species does not appear to undergo fluorosulfate exchange with the solvent, but the observed proton exchange would affect the self-ionization equilibrium

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \qquad (5)$$

Since electrical conductance in HSO_3F is best rationalized by the proton-jump mechanism,[21] the self-ionization ions $H_2SO_3F^+$ and SO_3F^- exhibit by far the greatest mobility, allowing meaningful electrical conductivity measurements over a limited concentration range. Of the hexakis(fluorosulfato)platinates, $(ClO_2)_2[Pt(SO_3F)_6]$ is selected as solute for such concentration-dependent electrical conductance studies because ClO_2 salts of this type are generally very soluble in fluorosulfuric acid, and similar studies on $(ClO_2)_2[Sn(SO_3F)_6]$[16] and $(ClO_2)_2[Ir(SO_3F)_6]$[22] and quite recently on $(ClO_2)_2[Ge(SO_3F)_6]$[11] have been reported by us.

The plot of specific conductance κ in Ω_{-1} cm^{-1} vs. concentration up to 2.6×10^{-2} mol kg^{-1} shows indeed a very similar straight line with a slightly steeper slope than had been found for the tin(IV)[16] and the iridium(IV) analogues,[22] characteristic of basic behavior. It appears that initial ionic dissociation according to

$$(ClO_2)_2[M(SO_3F)_6] \xrightarrow{HSO_3F} 2ClO_2^+(solv) + [M(SO_3F)_6]^{2-}(solv) \qquad (6)$$

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Table IV. Interpolated Specific Conductivities of $Pt(SO_3F)_4$, $Cs[Pt(SO_3F)_5]$, and $(ClO_2)_2[Pt(SO_3F)_6]$ in HSO_3F at 25.0 °C

$10^4 \times$ [solute], mol kg^{-1}	$10^4\kappa$, Ω^{-1} cm^{-1}		
	$Pt(SO_3F)_4$	Cs-$[Pt(SO_3F)_5]$	$(ClO_2)_2$-$[Pt(SO_3F)_6]$
0.000	1.134	1.148	1.720
0.002	11.83	3.537	5.185
0.004	12.43	5.925	7.986
0.006	16.05	8.273	10.59
0.008	22.05	10.62	13.54
0.010	28.05	12.63	15.54
0.012	32.85	14.64	17.82
0.014	37.08		20.11
0.016	41.73		22.29
0.018	46.78		24.59
0.020	51.58		27.46
0.022	56.03		30.43
0.024	60.25		32.86
0.026	64.41		34.10
0.028	68.50		
0.030	72.44		
0.032	76.31		
0.034	80.14		
0.036	83.96		
0.038	87.77		
0.040	91.57		

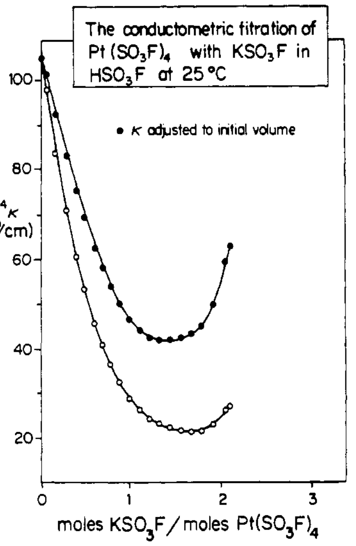

Figure 2.

with M = Sn, Ir, Ge, or Pt, is followed by two proton-transfer steps between solvent and solute, resulting in the equilibria

$$[M(SO_3F)_6]^{2-}(solv) + HSO_3F \rightleftharpoons H[M(SO_3F)_6]^{-}(solv) + SO_3F^{-}(solv) \quad (7)$$

$$H[M(SO_3F)_6]^{-}(solv) + HSO_3F \rightleftharpoons H_2[M(SO_3F)_6](solv) + SO_3F^{-}(solv) \quad (8)$$

Measured specific conductance values suggest formation of approximately 0.5 mol of SO_3F^-/mol of solute.

A different situation is encountered for solutions of $Pt(SO_3F)_4$ in fluorosulfuric acid. No comparison to other $M(SO_3F)_4$ species is possible, because $Sn(SO_3F)_4$ is virtually insoluble in HSO_3F[15] at 25 °C, the germanium analogue is unknown,[11] and solutions of $Ir(SO_3F)_4$ is HSO_3F have so far not been investigated in this respect.

The specific conductance data obtained on solutions of $Pt(SO_3F)_4$ in HSO_3F at 25.0 °C are listed in Table IV, together with κ values for $Cs[Pt(SO_3F)_5]$ and $(ClO_2)_2[Pt(SO_3F)_6]$. As can be seen from Figure 2, the conductometric titration curve suggests that $Pt(SO_3F)_4$ behaves as an acid in HSO_3F. In analogy to a formulation used in the $Au(SO_3F)_3$–HSO_3F system,[4] initial reaction with fluorosulfuric acid, according to

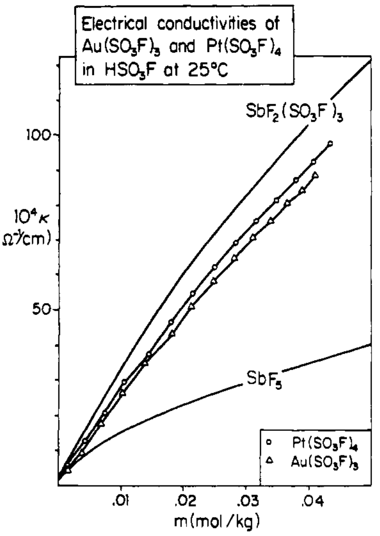

Figure 3.

$$Pt(SO_3F)_4 + 2HSO_3F \rightarrow H_2[Pt(SO_3F)_6](solv) \quad (9)$$

is followed by stepwise proton transfer to HSO_3F and the generation of the acidium ion $H_2SO_3F^+$ in solution via

$$H_2[Pt(SO_3F)_6](solv) + HSO_3F \rightleftharpoons H[Pt(SO_3F)_6]^{-}(solv) + H_2SO_3F^{+}(solv) \quad (10)$$

and a second proton-transfer step

$$H[Pt(SO_3F)_6]^{-}(solv) + HSO_3F \rightleftharpoons [Pt(SO_3F)_6]^{2-}(solv) + H_2SO_3F^{+}(solv) \quad (11)$$

Again the magnitude of κ, considering also the higher virtual mobility of $H_2SO_3F^+$ suggested by the proton-jump mechanism, indicates that equilibrium 10 appears to dominate with $H[Pt(SO_3F)_6]^-$ and $H_2[Pt(SO_3F)_6]$ as the principal platinum-containing species.

The conductometric titration with KSO_3F as standard base follows the overall reaction equation

$$H_2[Pt(SO_3F)_6] + 2KSO_3F \rightarrow K_2[Pt(SO_3F)_6] + 2HSO_3F \quad (12)$$

characteristic of a dibasic acid. The slope of the titration curve in Figure 2 reveals the initial electrical conductance, due to $H_2SO_3F^+$, decreases steeply to a base to acid mole ratio of ~1.0. On further KSO_3F addition, the curve becomes rather shallow. A conductivity minimum is found at an approximate base to acid mole ratio of 1.8 with a sharp break at 2.0 when all acidium ions have been consumed, and conductance beyond this point is then mainly due to the SO_3F^- ion.

Not unexpectedly, solutions of $Cs[Pt(SO_3F)_5]$ are weakly acidic. Only a qualitative test with addition of KSO_3F was undertaken to establish acid behavior, because the titration of the related $K[Sn(SO_3F)_5]$ with KSO_3F has recently been reported.[11]

It appears, then, that the species present in a solution of HSO_3F are the acid $H_2[Pt(SO_3F)_6]$ and its two anions $H[Pt(SO_3F)_6]^-$ and $[Pt(SO_3F)_6]^{2-}$, representing the first and second dissociation steps. All three species are connected by proton-transfer equilibria involving the solvent HSO_3F as outlined above. The three types of solutes studied, $Pt(SO_3F)_4$, $Cs[Pt(SO_3F)_5]$, and $Cs_2[Pt(SO_3F)_6]$, will form in solution primarily $H_2[Pt(SO_3F)_6]$, $H[Pt(SO_3F)_6]^-$, and $[Pt(SO_3F)_6]^{2-}$, respectively, capable of acidic, weakly acidic, or basic reaction in HSO_3F.

A plot shown in Figure 3 allows comparison of the principal acids in HSO_3F, $Au(SO_3F)_3$,[4] SbF_5,[23] and $SbF_2(SO_3F)_3$,[23] which is commonly regarded as the strongest acid in HSO_3F.[24] If it is assumed that electrical conductance is predominantly caused by the acidium ion $H_2SO_3F^+$, the relative slopes represent an approximate order of acidity. While seemingly not quite as acidic as the HSO_3F–SbF_5–$3SO_3$ system, the HSO_3F–$Pt(SO_3F)_4$ system has some definite advantages, such as (a) chemical simplicity reflected in the ^{19}F NMR spectrum, (b) thermal stability, (c) absence of byproducts, such as free SO_3, capable of causing side reactions, and (d) a reasonable resistance toward reducing or oxidizing agents. The HSO_3F–$Au(SO_3F)_3$ system shares all these positive features, as well as the singular but obvious disadvantage, the rather high price of the respective metals, which may limit their extensive use.

Acknowledgment. Financial support by the Natural Sciences and Engineering Council of Canada is gratefully acknowledged.

Registry No. $Pt(SO_3F)_4$, 36721-98-9; $Cs_2[Pt(SO_3F)_6]$, 90030-04-9; $(ClO_2)_2[Pt(SO_3F)_6]$, 90030-03-8; $Ba[Pt(SO_3F)_6]$, 71691-08-2; $(Br_3)_2[Pt(SO_3F)_6]$, 90046-22-3; $Cs[Pt(SO_3F)_5]$, 90030-05-0; Pt, 7440-06-4; $S_2O_6F_2$, 13709-32-5.

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University of Hong Kong, Hong Kong

Structural and Mechanistic Studies of Coordination Compounds. 39. Successful Application of the Marcus Theory in Predicting Rate Constants of Some Outer-Sphere Reductions of *trans*-Dihalogenotetraamineruthenium(III) Cations by Europium(II)

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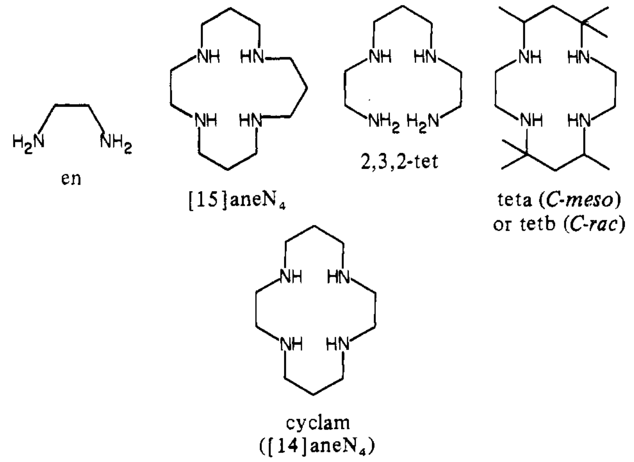
The kinetics of the europium(II) reduction of *trans*-$[Ru(en)_2X_2]^+$ (en = ethane-1,2-diamine; X = Cl, Br, I) and *trans*-$[RuLCl_2]^+$ [L = 2,3,2-tet (3,7-diazanonane-1,9-diamine), cyclam (1,4,8,11-tetraazacyclotetradecane), [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane), teta or tetb (*C-meso*- or *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, respectively)] has been studied at 25.0 °C in aqueous acidic solutions. From the Marcus cross-reaction relationship, self-exchange rate constants of some *trans*-$[RuLX_2]^{+/0}$ (X = Cl, Br) and $Eu_{aq}{}^{3+/2+}$ couples have been estimated. For the $Eu_{aq}{}^{3+/2+}$ couple, the estimated rate constants have been found to fall within the range of 2.3×10^{-4} to 1.7×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ at 25.0 °C and $\mu = 0.50$ mol dm^{-3}. The Marcus theory is found to be reasonably successful in predicting the rate constants for these cross-reactions.

Introduction

As part of our program to examine the chemistry of ruthenium(III) amine complexes, we have reported the chromium(II) and vanadium(II) reductions of some *trans*-$[Ru(tetraamine)X_2]^+$ (X = Cl, Br, I) cations.[1,2] Two distinct pathways, inner-sphere by chromium(II) and outer-sphere by vanadium(II), were clearly demonstrated. We report here the europium(II) reduction of *trans*-$[Ru(en)_2X_2]^+$ (en = ethane-1,2-diamine; X = Cl, Br, I) and *trans*-$[RuLCl_2]^+$ [L = 2,3,2-tet (3,7-diazanonane-1,9-diamine), cyclam (1,4,8,11-tetraazacyclotetradecane), [15]aneN_4 (1,4,8,12-tetraazacyclopentadecane), teta (*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), or tetb (*C-rac* isomer of teta)] (Chart I). The Marcus cross-reaction relationship[3] was employed to estimate the self-exchange rate constants of some *trans*-$[RuLX_2]^{+/0}$ and $Eu_{aq}{}^{3+/2+}$ couples.

Chart I



Experimental Section

The complexes reported here were prepared according to published methods.[4,5] Europium(II) solutions were prepared from amalgamated zinc reduction of europium(III) carbonate (Alfa) in toluene-*p*-sulfonic acid under an atmosphere of argon. Europium(II) was analyzed by oxidizing with deoxygenated iron(III) and determining the reduced iron(II) with acid dichromate. The ionic strength was maintained with sodium toluene-*p*-sulfonate.

Kinetic measurements were made on an Aminco-Morrow stopped-flow spectrophotometer equipped with an Aminco DASAR (data acquisition, storage, and retrieval) system. Experimental details on data collection, temperature control, and data treatment have been described previously.[6] All operations were carried out under deoxygenated argon. Syringe techniques were used for the transfer of air-sensitive solutions.

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