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FLUOROSULFATES OF THE NOBLE METALS, PART 4[a] FLUOROSULFATES OF IRIDIUM

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SUMMARY

The synthesis of the binary fluorosulfates $Ir(SO_3F)_3$ and $Ir(SO_3F)_4$ and of the ternary fluorosulfates $(ClO_2)_2[Ir(SO_3F)_6]$, $Cs_2[Ir(SO_3F)_6]$ and $Ba[Ir(SO_3F)_6$ is described. The preparative runs are characterized by long reaction times, often up to several weeks, even at elevated temperatures, due to the relative inertness of iridium towards the strongly oxidizing reaction mixture of bis(fluorosulfuryl)-peroxide, $S_2O_6F_2$, and fluorosulfuric acid, HSO_3F. Structural characterizations are based on infrared spectra and in case of the Ir(IV) compounds on temperature dependant magnetic susceptibility measurements. The magnetic moments μ_{eff} obtained are slightly below the calculated values suggesting weak antiferromagnetic coupling.

INTRODUCTION

In the course of a systematic study of the fluorosulfates of the noble metals [1] to [3], we became interested in a study of both binary and ternary fluorosulfates of iridium. In preceding studies [2], [4], we had found the metal oxidation by bis(fluorosulfuryl)peroxide, $S_2O_6F_2$, with fluorosulfuric acid, HSO_3F, as reaction medium to provide a fast and

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a) The preceding three publications in this series were published under the heading: Fluorosulfates of Palladium Parts I to III. See ref [1] to [3].

efficient route to both classes of compounds, according to the schemes

$$M + {}^{n}/_{2}\ S_2O_6F_2 \xrightarrow{HSO_3F} M(SO_3F)_n \text{ and} \qquad (1)$$

$$m\ M'SO_3F + M + {}^{n}/_{2}\ S_2O_6F_2 \xrightarrow{HSO_3F} M'_m\ [M(SO_3F)_{n+m}] \qquad (2)$$

with M' = Cs, K or ClO_2 as well as others. In case of the alkali metal fluorosulfates, the reaction of chlorides or bromides with HSO_3F was found to result in a simple, one step synthesis of ternary fluorosulfates *in situ*:

$$m\ M'Cl + M + {}^{n}/_{2}S_2O_6F_2 + m\ HSO_3F \xrightarrow[-mHCl]{HSO_3F} M'_m[M(SO_3F)_{n+m}] \qquad (3)$$

The role of fluorosulfuric acid in these reactions was found to be two-fold: a) the excellent solvolysing ability of HSO_3F was found [4] to accelerate reactions by effectively preventing surface coating on the metal, and b) the wide liquid range of HSO_3F with a normal boiling point of +163°C made it possible to achieve and maintain reaction temperatures up to 160°C. The use of glass reaction vessels must be viewed as an advantage, even though elevated temperatures and prolonged reaction times were found to result in some etching of the reaction vessels, often affecting the weights obtained when following these reaction quantitatively.

We became interested to test the synthetic routes described above by selecting with iridium a metal, which had in the past displayed great resistance towards oxidizing agents [5].

EXPERIMENTAL

Chemicals

Iridium metal powder, 60 mesh of 99.9% purity was obtained from the Ventron Corporation. Technical grade fluorosulfuric acid (Allied Chemicals) was double distilled at atomospheric pressure as described previously [6]. Bis(fluorosulfuryl)peroxide [7] and chloryl fluorosulfate [8] were synthesized according to published methods. All other chemicals used in this study were obtained from commercial sources in the highest purity degree available.

Instrumentation and Analysis

Details on our instrumentation and the techniques employed in manipulating volatile and moisture sensitive substances, the recording of infrared, Raman and electronic spectra and the calibration of magnetic susceptibility measurements have been published previously [2]. The Gouy apparatus used in this study has been described earlier [9]. Diamagnetic corrections were calculated from Pascals constants [10]. Magnetic data on other iridium compounds was obtained from reference [10].

All reactions were performed in Pyrex reaction vials of about 40 ml contents fitted with Kontes Teflon stem valves and Teflon coated magnetic stirring bars. The course of reactions was monitored by recording weight changes of the nonvolatile products. Microanalyses were performed by Analytische Laboratorien, Elbach, West Germany.

Synthetic Reactions

Iridium tris(fluorosulfate)

$$Ir + 2S_2O_6F_2 \xrightarrow{HSO_3F} Ir(SO_3F)_4 \qquad (4)$$

$$Ir(SO_3F)_4 \xrightarrow[\Delta]{+\ 120°C} Ir(SO_3F)_3 + {}^1/_2 S_2O_5F_2 + {}^1/_2 O_2 \qquad (5)$$

In a typical reaction, iridium metal (158 mg, 0.822 mmol) was treated with an excess of $S_2O_6F_2$/HSO_3F (∿10 ml) at ∿140°C. Parts of the metal initially dissolved to form a brown solution containing $Ir(SO_3F)_4$; after 3 days of heating, a deep purple solution together with unreacted metal was formed. After the removal of most of the $S_2O_5F_2$ and oxygen formed from the reaction, more $S_2O_6F_2$ (∿3 ml) was added to the mixture which was subsequently reheated at ∿140°C. After 3 days, all metal had dissolved and the solution reverted to a deep purple color. Volatile materials were removed in vacuo and a solid which analyzed as $Ir(SO_3F)_3$ was obtained, (398 mg, 0.813 mmol). $Ir(SO_3F)_3$ was also obtained by the thermal decomposition of $Ir(SO_3F)_4$ at ∿120°C in vacuo according to equation (5). In a typical pyrolysis experiment, $Ir(SO_3F)_4$ (294 mg, 0.500 mmol) was converted into $Ir(SO_3F)_3$ (239 mg, 0.488) after 12 hours of heating.

$Ir(SO_3F)_3$ is a very deep bluish purple, hygroscopic solid. It dissolves in HSO_3F and decomposes at ∿200°C with the evolution of a colorless gas which was not identified.

Analysis:	Ir	S	F
Calculated %	39.27	19.66	11.65
Found %	39.10	19.46	11.48

Infrared absorption bands in cm^{-1} with estimated relative intensities: 1400s, 1210s, 1100vs, b, 1020vs, sh, 950s, b, 800s, vb, 630s, 575ms, 540m and 450m.

Iridium tetrakis(fluorosulfate)

$$Ir(SO_3F)_3 + 1/2S_2O_6F_2 \rightarrow Ir(SO_3F)_4 \qquad (6)$$

$Ir(SO_3F)_4$ is prepared in a reaction similar to that above. Iridium metal (198 mg, 1.030 mmol), was treated with $S_2O_6F_2/HSO_3F$ (∿4 ml) using similar cycles of $S_2O_6F_2$ addition. When all the metal had dissolved and most of the $S_2O_5F_2$ had been removed, $S_2O_6F_2$ (∿2 ml) was added to the solution of essentially $Ir(SO_3F)_3$ in HSO_3F. This was heated at +60°C for 6 hours, after which time a deep brown solution had formed. The removal of all volatile materials by the usual method yielded $Ir(SO_3F)_4$ with traces of the blue $Ir(SO_3F)_3$ (the weight of the product was slightly lower than expected for $Ir(SO_3F)_4$). More $S_2O_6F_2$ (∿2 ml) was added to this impure product which was heated at 60°C for another 6 hours. The removal of all excess $S_2O_6F_2$ (and traces of $S_2O_5F_2$ and oxygen) at room temperature yielded pure $Ir(SO_3F)_4$ (607 mg, 1.032 mmol).

$Ir(SO_3F)_4$ is a deep brown, almost black, hygroscopic solid which is very soluble in HSO_3F. It decomposes into $Ir(SO_3F)_3$ according to equation (5) at ∿100°C in vacuo but is stable up ∿150°C in an atmosphere of N_2.

Analysis:	Ir	S	F
Calculated %	32.66	21.80	12.92
Found %	32.50	21.60	12.69

Infrared absorption bands in cm^{-1} and relative estimated intensities: 1390, s, 1210s, 1070s, sh, 1020s, b, 870s, b, 820s, b, 640m, b, 580m and 540m.

$\underline{(ClO_2)_2[Ir(SO_3F)_6]}$

$$2ClO_2SO_3F + Ir + 2S_2O_6F_2 \xrightarrow{HSO_3F} (ClO_2)_2[Ir(SO_3F)_6] \qquad (7)$$

A mixture of ClO_2SO_3F (∿1 ml), and $S_2O_6F_2/HSO_3F$ (∿6 ml) was allowed to react with iridium metal (289 mg, 1.505 mmol) at ∿120°C for 3 days. All the metal by that time had dissolved and the solution became dark brown. The removal of all volatile materials at +70°C yielded a compound which analyzed as $(ClO_2)_2[Ir(SO_3F)_6]$ (1,362 g, 1.478 mmol).

$(ClO_2)_2[Ir(SO_3F)_6]$ can also be prepared by:

a) replacing ClO_2SO_3F with $ClSO_3F$ in reaction scheme (7) and proceeding under similar conditions, or

b) treating $IrCl_3$ with $S_2O_6F_2/HSO_3F$ at ∿120°C for 4 days. In both these synthetic routes, the required ClO_2SO_3F is generated by an attack of $ClSO_3F$ (formed from the reaction of $IrCl_3$ with $S_2O_6F_2$ in (b)) on the glass reactor.

$(ClO_2)_2[Ir(SO_3F)_6]$ is a dark orange-brown, hygroscopic solid. It is soluble in HSO_3F and melts with decomposition at +190°C to form a dark brown liquid.

Analysis :	Cl	Ir	F
Calculated %	7.69	20.68	12.37
Found %	7.51	21.04	12.44

$\underline{Cs_2[Ir(SO_3F)_6]}$

$$CsCl + HSO_3F \longrightarrow CsSO_3F + HCl \qquad (8)$$

$$2CsSO_3F + Ir + 2S_2O_6F_2 \xrightarrow{HSO_3F} Cs_2[Ir(SO_3F)_6] \qquad (9)$$

$Cs_2[Ir(SO_3F)_6]$ was prepared by the oxidation of iridium metal (398 mg, 2.071 mmol with $S_2O_6F_2/HSO_3F$ (∿10 ml) in the presence of CsCl (798 mg, 4.146 mmol) at ∿150°C for 10 days. The removal of all volatile materials at ∿70°C yielded a product with a weight correponding to that expected for $Cs_2[Ir(SO_3F)_6]$, (2.121 g, 2.015 mmol).

$Cs_2[Ir(SO_3F)_6]$ is a pale orange, hygroscopic solid. It is soluble in HSO_3F and melts with decomposition at +150°C.

Preparation of $Ba(Ir(SO_3F)_6]$

$$BaCl_2 + 2HSO_3F \longrightarrow Ba(SO_3F)_2 + HCl \tag{10}$$

$$Ba(SO_3F)_2 + Ir + 2S_2O_6F_2 \xrightarrow{HSO_3F} Ba[Ir(SO_3F)_6] \tag{11}$$

A mixture of dried $BaCl_2$ (198 mg, 0.951 mmol) and iridium metal (183 mg, 0.952 mmol) was treated with $S_2O_6F_2/HSO_3F$ (∿10 ml) at ∿100°C for 2 weeks and, after replenishing the largely decomposed $S_2O_6F_2$, at ∿160°C for another 2 weeks. The removal of all volatile materials at ∿70°C yielded a product with a weight suggesting the composition of $Ba[Ir(SO_3F)_6]$ (788 mg, 0.853 mmol). The low yield is due to the visually evident etching of the glass reactor by the solution.

$Ba[Ir(SO_3F)_6]$ is a light orange, hygroscopic solid. It appears to be almost insoluble in HSO_3F, and decomposes at ∿200°C.

RESULTS AND DISCUSSION

Synthesis

Of all the 4d and 5d block metals so far studied, iridium was found to show the greatest resistance towards oxidation by $S_2O_6F_2$, with the possible exception of rhodium [11]. Attempts to replace the metal by $IrCl_3$ resulted in no improvement and quite often in incomplete reactions.

The preparative reactions described could take up to 1 month for completion, while some had to be aborted eventually due to extensive glass attack caused by irreversible decomposition of both the reactant

($S_2O_6F_2$) and the solvent (HSO_3F). A higher reaction temperature (>160°) was not feasible since decomposition took place much faster than the conversion of the metal to either Ir(III)- or Ir(IV)- species. The $S_2O_5F_2$ formed, identified by i.r. spectroscopy, had to be removed before the $S_2O_6F_2$ could be replenished because its presence reduces the ionizing ability of the solvent. Because of the extremely dark colors of the solutions, the addition of the oxidant was usually repeated at least twice after all the metal had visibly disappeared, to ensure complete reaction.

The limited thermal stability of $Ir(SO_3F)_4$ presented an additional complication. Its decomposition into $Ir(SO_3F)_3$ with formation of O_2 and disulfuryl difluoride, $S_2O_5F_2$, according to equation (5), followed by reoxidation and decomposition cycles, accounted for the consumption of the oxidizer and the pressure build up during reactions. Normally at elevated temperatures $S_2O_6F_2$ had been found to dissociate reversibly into fluorosulfate radicals [12]:

$$S_2O_6F_2 \rightleftharpoons 2\cdot SO_3F \qquad (12)$$

These difficulties also affected the synthesis of complexes containing the $[Ir(SO_3F)_6]^{2-}$ ion. This species appeared to dissociate far more readily in solution than in the solid state. $Ba[Ir(SO_3F)_6]$, which did not dissolve appreciably in HSO_3F even at elevated temperatures, could be obtained at reaction temperatures of +160°C, but attempts to synthesize a presumably more soluble $Na_2[Ir(SO_3F)_6]$ had to be abandoned after one month due to extensive corrosion of the reaction vessel. Evidence for such corrosion was found in the weights of the final reaction products, which were always lower than expected (see Experimental section). Attempts to obtain fluorosulfate complexes of Ir(III) were unsuccessful.

In summary the reactions described here pointed clearly to the limitations of our synthetic method. All reactions were extremely time consuming and required rather large quantities of bis(fluorosulfuryl)peroxide. The formation of oxygen during the reactions required constant monitoring in order to avoid explosion.

Vibrational Spectra

Due to the intense dark colours of both binary fluorosulfates Raman spectra could not be obtained. Infrared spectra were of extremely poor resolution and use of fluorocarbon oils as mulling agents resulted in no improvement. The observed band positions have been listed in the experimental section without interpretation.

For the $[Ir(SO_3F)_6]^{2-}$ complexes, i.r. spectra of reasonable resolution could be obtained, but due to their deep yellow color Raman spectra of only relatively poor quality were recorded at 80 K [13]. The vibrational frequencies of these compounds are listed in Table 1 in comparison with the Raman frequencies of $Cs_2[Pt(SO_3F)_6]$. [14]. The three iridium complexes have spectra that are similar to that of $Cs_2[Pt(SO_3F)_6]$, suggesting a similar type of metal-ligand interaction and a monodentate coordination of the SO_3F-groups. The positions of the three vibrational modes of ClO_2^+ at (1310, 1295), 1060 and 522 cm^{-1} in the i.r. spectrum indicate an ionic formulation for the compound.

In summary, it appears that all the iridium species involved in this study have octahedral coordination for iridium, with bidentate SO_3F-groups evident for the two binary fluorosulfates.

Magnetic Susceptibility Measurements

Not unexpectedly $Ir(SO_3F)_3$ is found to be diamagnetic, suggesting a spin paired d^6 system. However the experimental χ_m value of $(-80\pm30)\times10^{-6}$ cm^3 mol^{-1}, suggests by comparison with the calculated value of -154×10^{-6} cm^3 mol^{-1} a small contribution from temperature independent paramagnetism (TIP). Similar TIP contributions have been observed for both the rhombic and the monoclinic forms of $IrCl_3$ [10].

TABLE 1

Vibrational frequencies of $[Ir(SO_3F)_6]^{2-}$ complexes.

$(ClO_2)_2[Ir(SO_3F)_6]$		$Cs_2[Ir(SO_3F)_6]$		$Ba[Ir(SO_3F)_6]$	$Cs_2[PtSO_3F)_6]$
IR	R^+	IR	R	IR	R
1400s,b	1400,1380w	1390sb	1415w	1390s	1416w,sh 1410m
1310s*					
1295s*					
	1250vs		1255m		1250vs
1200s	1200w	1195s,b	1212w	1200s	1219m
1050w*	1047s*				
			1057m		1043s
950vs,vb		950vs,b	978w	950s,b	1010m
		920vs,b	950w	900s,b	
820s	840,810w	-800s,b	-802w,b	820s	∿800w,b
660s	640w	645m	630w	630w	634vs
590s	580w	570s	575w	575m	579vw
550s	548w	540s	550w	540m	550vw
522m*	520w*				
	460w	460w		460w,sh	
	443w	440m	440w	447m	440m
	286m		287w		280vs
	268m				

* denotes bands due to ClO_2^+

$^+$ obtained at 80k

IR denotes infrared band positions, R denotes Raman shifts.

For $Ir(SO_3F)_4$ and its derivatives a spin paired d^5 system would result in a $^2T_{2g}$ groundstate, an assumption seemingly justified for the hexakis(fluorosulfato)iridate (IV) complexes. According to Figgis, the magnetic susceptibility of a d^5 low spin system with a $^2T_{2g}$ electronic ground state can be represented by the equation [15]:

$$\mu^2 = \frac{8 + (3x - 8)\exp(-3x/2)}{x[2 + \exp(-3x/2)]} \qquad (13)$$

where $x = \lambda/kT$

$\lambda = -\xi = -5000\ \mathrm{cm}^{-1}$ for Ir(IV) [5] = spin orbit coupling constant,

k = Boltzmann's constant = $0.6950\ \mathrm{cm}^{-1}$

This would imply, as x approaches ∞, (for large $|\lambda|$ values or at very low temperatures) μ would approach $\sqrt{3}$, while as $x \longrightarrow 0$, the magnetic moment may approach a value of $\sqrt{5}$.

In the temperature range accessible in this study (∿100 to 330 K), μ should have values from 1.76 μ_B at 100 K to 1.84 μ_B at 330 K. For the hexachloro- and hexabromocomplexes of Ir(IV), μ_{eff} was found to generally decrease with temperature, but in most cases they were lower than $\sqrt{3}$, the minimum value predicted by equation (13). The moments also showed marked drops at temperatures below ∿150 K to ∿1.3 μ_B; this had been attributed to antiferromagnetic coupling in the system [10].

The magnetic susceptibility results on $(ClO_2)[Ir(SO_3F)_6]$ $Cs_2[Ir(SO_3F)_6]$ and $Ir(SO_3F)_4$ are listed in Table 2 respectively. The temperature dependence of their μ_{eff} is shown in Fig. 1.

In all three cases, the observed magnetic moments are lower than the expected values (the estimated uncertainty in μ is about $\pm 0.02\mu_B$).

The difference is most pronounced for the magnetic moments found for $Ir(SO_3F)_4$ and the discussion will center primarily on the two hexakis(fluorosulfato)iridate(IV) compounds. The observed cation dependance of μ is also found for salts containing the $[IrCl_6]^{2-}$ ion [11], [16].

As can be seen from Fig. 1, the magnetic moments are relatively independent of temperature and the Curie-Weiss law seems to be followed for T>150 K. This gives $1/\chi_m^c$ values as shown in Table 2, implying approximate Weiss constants between 12 and 28K.

The magnetic behavior found may best be rationalized by assuming antiferromagnetic coupling, an explanation also favoured for the $[IrCl_6]^{2-}$ salts.

TABLE 2

Magnetic properties of $(ClO_2)_2[Ir(SO_3F)_6]$, $Cs_2[Ir(SO_3F)_6]$ and $Ir(SO_3F)_4$

	T [K]	$\chi_m^c \times 10^3$ [cm^3 mol]	$1/\chi_m^c$ [cm^{-3} mol]	χ_m^c a) [cm^{-3} mol]	μ_{eff} [μ_B]	μ_{eff} a) [μ_B]
$(ClO_2)_2[Ir(SO_3F)_6]$	78	4.348	230	234	1.64	1.63
	108	3.236	309	314	1.67	1.66
	130	2.653	377	371	1.66	1.67
$1/\chi_m^c$(calc'd) =	155	2.294	436	436	1.68	1.68
	178	2.000	500	498	1.69	1.69
(T+12)/0.382	203	1.770	565	563	1.70	1.70
	227	1.585	631	626	1.70	1.70
	251	1.447	691	689	1.70	1.71
	276	1.326	754	755	1.71	1.71
	300	1.238	808	816	1.72	1.71
$Cs_2[Ir(SO_3F)_6]$	78	3.831	261	269	1.55	1.52
	106	3.003	333	339	1.59	1.58
	129	2.494	401	399	1.60	1.61
$1/\chi_m^c$ (calc'd) =	154	2.141	467	462	1.62	1.63
	179	1.880	532	524	1.64	1.65
(T+28)/0.395	203	1.681	595	586	1.65	1.66
	229	1.536	651	651	1.68	1.68
	252	1.410	709	709	1.68	1.68
	277	1.290	775	773	1.69	1.69
	302	1.214	824	836	1.71	1.70
$Ir(SO_3F)_4$	284	0.906	1104	1155	1.43	1.40
	254	0.963	1039	1040	1.40	1.40
	230	1.028	972.9	948.9	1.38	1.39
$1/\chi_m^c$ (calc'd) =	205	1.102	907.7	853.5	1.34	1.39
	177	1.302	757.5	746.7	1.37	1.38
(T+19)/0.262	154	1.556	642.8	659.0	1.38	1.37
	130	1.758	569.1	567.5	1.35	1.35
	107	2.044	489.3	479.8	1.32	1.34
	78	2.963	337.5	369.1	1.36	1.30

Explanation: T = temperature of measurement in K; χ_m^c = molar magnetic susceptibility, corrected for diamagnetism in cm^3 mol^{-1},
μ_B = Bohr Magneton, μ_{eff} = effective magnetic moment
a) calculated values

The possibility of antiferromagnetic coupling, was therefore investigated further. As the vibrational spectra of the $[Ir(SO_3F)_6]^{2-}$ and $[Pt(SO_3F)_6]^{2-}$ complexes show great similarities, and similar structures as expected, a dilution experiment involving a mixture of $(ClO_2)_2[M(SO_3F)_6]$, M=Ir,Pt, was undertaken.

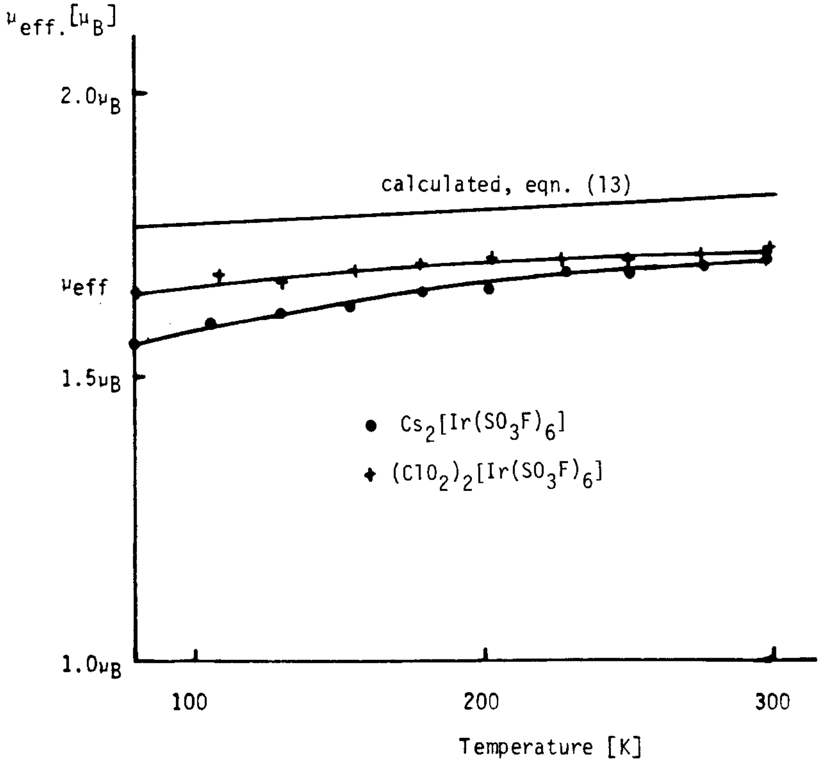

FIG. 1. MAGNETIC MOMENTS OF $(ClO_2)_2[Ir(SO_3F)_6]$ AND $Cs_2[Ir(SO_3F)_6]$

Starting with a mixture of metal powders containing 8.85 mole % of iridium, the mixed chloronium salt was prepared by reacting the metals with ClO_2SO_3F and $S_2O_6F_2/HSO_3F$. The resulting product has the expected weight and had the appearance of $(ClO_2)_2[Pt(SO_3F)_6]$. The result of a bulk magnetic susceptibility measurement on the mixture is given in Table 3.

The ClO_2-containing complexes were used because, in the case of $[Ir(SO_3F)_6]^{2-}$, it is the only iridium complex that can be prepared comparatively easily. The presence of an excess of ClO_2SO_3F, also ensures the formation of a highly pure product. The diamagnetic correction of (250 15)x10^{-6} cgs units, obtained for $(ClO_2)_2[Pt(SO_3F)_6]$ over a temperature range of 81 to 300 K, was used for both the complexes.

TABLE 3

Magnetic properties of $(ClO_2)_2[Ir(SO_3F)_6]$ diluted in $(ClO_2)_2[Pt(SO_3F)_6]$ (8.85 mol% Ir)

T [K]	$\chi_m^c \times 10^3$ [$cm^3 mol^{-1}$]	$1/\chi_m^c$	$1/\chi_m^c$ (calc.)	μ_{eff} [μ_B]	μ_{eff}(calc) [μ_B]
303	1.506	664	728	1.91	1.82
277	1.515	660	675	1.83	1.81
251	1.435	697	621	1.70	1.80
229	1.616	619	575	1.72	1.78
204	1.911	523	523	1.77	1.76
179	2.201	454	472	1.78	1.74
154	2.416	414	420	1.73	1.71
129	2.745	364	369	1.68	1.67
106	3.073	325	320	1.61	1.62
78	4.049	247	263	1.59	1.54

Any Temperature Independent Paramagnetism present in these systems, estimated to be of the order of only 50×10^{-6} cm^3 mol^{-1} [15] should be compensated for by this procedure.

Although the accuracy of the measurements is greatly reduced by the introduction of the diamagnetic species $(ClO_2)_2[Pt(SO_3F)_6]$, as the majority constituent (the estimated uncertainty, arising mainly from weight measurements, ranges from ±0.12 μ_B at ~300 K to ±0.05 μ_B at 80 K), the values of μ_{eff} obtained agree well with those calculated from equation (13), and in general, are consistently higher than those of pure $(ClO_2)_2[Ir(SO_3F)_6]$. Thus antiferromagnetic coupling does occur in the Ir(IV) fluorosulfate system, and is the most likely cause contributing to a lowering of μ_{eff} in these compounds. Similarly the low μ_{eff} values for $Ir(SO_3F)_4$ may at least in part be due to antiferromagentic coupling, a process more likely in a polymeric, fluorosulfate bridged compound, than in the anionic complexes discussed above. While our data suggest strongly the presence of antiferromagnetism in these Ir(IV) compounds, an extension of the range of measurement down to 4 K would be required to be completely certain about the extent of such coupling.

Solution Studies in HSO_3F

The isolation and identification of the hexakis(fluorosulfato)-iridate(IV) complexes suggest that $Ir(SO_3F)_4$ may act as a fluorosulfate io acceptor:

$$Ir(SO_3F)_4 + 2SO_3F^- \rightleftharpoons [Ir(SO_3F)_6]^{2-} \qquad (14)$$

and possibly even as an ansolvo acid as does $Pt(SO_3F)_4$ [14]. However the difficulties in obtaining $Ir(SO_3F)_4$ present a substantial obstacle to detailed studies.

We have therefore restricted our studies to an exploratory investigation. The conductivity data listed in Table 4 suggest a simple ionic dissociation according to:

$$(ClO_2)_2[Ir(SO_3F)_6] \xrightleftharpoons{HSO_3F} 2ClO_2^+{}_{(solv)} + [Ir(SO_3F)_6]^{2-}{}_{(solv)} \qquad (15)$$

similar to results for $(ClO_2)_2[Pt(SO_3F)_6$, and suggest existence of $[Ir(SO_3F)_6]^{2-}$ in HSO_3F solution.

Interestingly $Ir(SO_3F)_4$ and $(ClO_2)_2[Ir(SO_3F)_6$ give identical absorption spectra in HSO_3F with a very intense band ($\varepsilon \sim 10000$) at 200 nm. Solutions of $Ir(SO_3F)_3$ show a similarly strong band with λ_{max} at 563 nm. It seems likely that these bands are due to ligand → metal charge transfer. Their intensity and broad band shape prevent the observation of bands due to d-d transitions.

TABLE 4

Conductivity of $(ClO_2)_2[Ir(SO_3F)_6]$ in HSO_3F^* at 25.0°C.

Conc. x 10^2 [mol x kg^{-1}]	κ(spec/cond.) x 10^4 [ohm^{-1} cm^{-1}]	Conc. x 10^2 [mol x kg^{-1}]	κ(spec/cond.) x 10^4 [ohm^{-1} cm^{-1}]
0.00	0.280	1.40	19.60
0.20	3.801	1.60	21.50
0.40	7.581	1.80	23.60
0.60	9.885	2.00	25.63
0.80	12.20	2.20	27.49
1.00	14.92	2.40	30.06
1.20	17.56	2.60	32.22

conc. in mol x kg^{-1} x 10^2 κ = specific conductance in ohm^{-1} cm^{-1}

* interpolated

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REFERENCES

1 K.C. Lee and F. Aubke, Canad. J. Chem. 55, 2473 (1977).

2 K.C. Lee and F. Aubke, Canad. J. Chem. 57, 2058 (1979).

3 K.C. Lee and F. Aubke, Canad. J. Chem. in press.

4 P.C. Leung and F. Aubke, Inorg. Chem. 17, 1765 (1978).

5 W.P. Griffith, The Chemistry of the Rarer Platinum Metals, Interscience - Wiley, New York (1968).

6 J. Barr, R.J. Gillespie and R.C. Thompson, Inorg. Chem. 3, 1149 (1964).

7 G.H. Cady and J.M. Shreeve, Inorg. Synth. 7, 124 (1963).

8 H.A. Carter, A.M. Qureshi and F. Aubke, Chem. Commun. 1461 (1968).

9 H.C. Clark and R.J. O'Brien, Canad. J. Chem. 39, 1030 (1961).

10 Landolt-Börnstein, Numerical data and functional relationships in science and technology, Vol. 2. Magnetic properties of coordination and organometallic transition metal compounds. Springer Verlag, Berlin, 1966.

11 G.B. Wong and F. Aubke, unpublished results.

12 F.B. Dudley and G.H. Cady, J. Amer. Chem. Soc. 85, 3375 (1963).

13 A suitable cell to obtain Raman spectra at 80 K has been described by us: K.C. Lee and F. Aubke, Canad. J. Chem. 57, 2058 (1979).

14 K.C. Lee and F. Aubke to be published. See also K.C. Lee, Ph.D. thesis, University of British Columbia, 1980.

15 B.N. Figgis, Introduction to Ligand Fields, Interscience,New York (1967).

16 V. Norman and J.C. Morrow III, J. Chem. Phys. 31, 455 (1959).