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Synthesis, Molecular Structure, and Vibrational Spectra of *mer*-Tris(carbonyl)iridium(III) Fluorosulfate, *mer*-$Ir(CO)_3(SO_3F)_3$

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Addition of carbon monoxide (0.5−2 atm) to iridium(III) fluorosulfate, $Ir(SO_3F)_3$, dissolved in HSO_3F over 4 days and at 60 °C, results in the quantitative formation of tris(carbonyl)iridium(III) fluorosulfate $Ir(CO)_3(SO_3F)_3$. Slow evaporation of the solvent produces single crystals of *mer*-$Ir(CO)_3(SO_3F)_3$. Crystal structure data for *mer*-$Ir(CO)_3(SO_3F)_3$: monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8.476(1)$ Å, $b = 12.868(2)$ Å, $c = 12.588$ (1) Å, $\beta = 108.24(1)°$, $V = 1304.0$ Å^3, $T = 200$ K, $R_F = 0.022$ for 2090 data ($I_o \geq 2.5\sigma(I_o)$) and 200 variables. Vibrational spectra of the crystalline solid are consistent with a *mer*-isomer with CO stretching modes at 2249 (A_1), 2208 (B_1), and 2198 (A_1) cm^{-1} in the IR spectrum. In solution of HSO_3F, additional CO stretching bands attributed to the *fac*-isomer are found in the FT-Raman and IR spectra at 2233 (A_1) and 2157 cm^{-1} (E). Additional evidence for a mixture of *fac*- and *mer*-isomers comes from ^{19}F NMR spectra. The vibrational spectra suggest strongly reduced iridium to CO π-back-bonding. The crystal structure reveals significant intra- and intermolecular contacts between the electropositive C atom of the CO groups and O or F atoms of the fluorosulfate groups. Hence *mer*-tris(carbonyl)iridium(III) fluorosulfate becomes the first thermally stable, structurally characterized, and predominantly σ-bonded carbonyl derivative of a metal in the +3 oxidation state.

Introduction

We have recently reported on the synthesis of three noble metal carbonyl fluorosulfates, $Au(CO)SO_3F$,[1] *cis*-$Pt(CO)_2(SO_3F)_2$[2] and *cis*-$Pd(CO)_2(SO_3F)_2$.[2] The latter compound has subsequently been structurally characterized by X-ray diffraction.[3] Vibrational analysis suggests the presence of covalent O-monodentate fluorosulfate groups and terminal CO groups trans to the fluorosulfate ligands.[1,2] However the $\bar{\nu}$(CO) stretching modes are shifted to higher wavenumbers relative to $\bar{\nu}$(CO(g)) (2143 cm^{-1}) and are observed at 2196 cm^{-1} for $Au(CO)SO_3F$,[1] 2185 and 2219 cm^{-1} for *cis*-$Pt(CO)_2(SO_3F)_2$,[2] and 2208 and 2228 cm^{-1} for *cis*-$Pd(CO)_2(SO_3F)_2$,[2] which in turn suggests substantially reduced π-back-donation.

The molecular structure of *cis*-$Pd(CO)_2(SO_3F)_2$[3] confirms our conclusion based on vibrational spectra and reveals in addition a number of significant intra- and intermolecular contacts between the carbon atom of the CO group and oxygen atoms of the fluorosulfate groups, which appear to stabilize the structure.

We have now extended our synthetic approach to iridium and report here the synthesis of tris(carbonyl)iridium(III) fluorosulfate, $Ir(CO)_3(SO_3F)_3$. Vibrational and ^{19}F-NMR spectra in HSO_3F solution suggest the initial formation of an isomeric mixture of the facial and meridional forms with the latter the major constituent. Polycrystalline samples, formed by rapid solvent removal are again a mixture of *mer*- and *fac*-$Ir(CO)_3(SO_3F)_3$ according to the vibrational spectra. However slow removal of HSO_3F allows the growth of single crystals. The subsequent molecular structure determination and vibrational spectra of the crystals indicate conclusively that in the crystalline solid only the meridional isomer is present and is apparently less soluble in HSO_3F than the *fac*-isomer. The opposite observation has recently been reported for $Ir(CO)_3F_3$[4] in a solution of anhydrous HF, where according to solution NMR at −78 °C (^{19}F and ^{13}C) and the IR spectrum of the isolated solid, the facial isomer is predominant. A *fac*-isomer is also suggested for $Ir(CO)_3I_3$.[5]

Experimental Section

(i) Chemicals. Iridium metal powder, 60 mesh of 99.9% purity, was obtained from the Ventron Corporation (Alfa Inorganics). Technical grade fluorosulfuric acid (Orange County Chemicals) was doubly distilled at atmospheric pressure as described previously.[6] Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, was obtained by the catalytic fluorination of SO_3 in a procedure[7] adopted from a previous report.[8] Iridium(III) fluorosulfate, $Ir(SO_3F)_3$ is obtained by oxidation of iridium metal with $S_2O_6F_2$ in HSO_3F at 120 to 140 °C. The earlier[9] report is substantially modified and details are described below. Carbon monoxide (CP grade 99.5% purity) was obtained from Linde Gases and passed through a glass trap cooled to 77 K, to retain moisture and other impurities.

(ii) Instrumentation. Infrared spectra were recorded on a Bomen MB 102 Fourier transform spectrometer. Solid samples were pressed as thin films between AgBr or AgCl (Harshaw Chemicals) windows. FT-Raman spectra were recorded on Bruker FRA 106 FT-Raman accessory mounted on an IFS 66v FT-IR optical bench.

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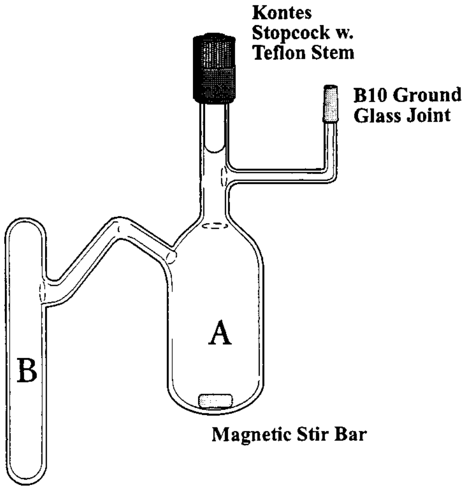

Figure 1. Two-part reactor used in the syntheses of $Ir(SO_3F)_3$ and $Ir(CO)_3(SO_3F)_3$.

^{19}F-NMR spectra were obtained on a Varian XL-300 FT multinuclear spectrometer operating at 282.231 MHz. About 10 mg of crystalline *mer*-$Ir(CO)_3(SO_3F)_3$ was dissolved in 0.5 mL of HSO_3F. $CFCl_3$ was used as external reference. The spectrum was acquired without a lock.

(iii)The Synthesis of $Ir(CO)_3(SO_3F)_3$. Iridium metal was oxidized, initially to $Ir(SO_3F)_4$, by reaction with a large excess of $S_2O_6F_2$ in HSO_3F at ~120 °C over several weeks as described previously.[9] To ensure complete oxidation of iridium a two-part reactor, shown in Figure 1, was employed. In a typical reaction 0.0976 g of metal powder was added *via* a funnel through the stopcock to part A of the reactor. About 2.5 mL each of HSO_3F and $S_2O_6F_2$ were added by distillation *in vacuo* to part A. The reaction mixture was heated to 120 °C with vigorous magnetic stirring for 16 h. Some of the metal was consumed at this stage to give a dark brown solution. The mixture was allowed to cool to room temperature and the unreacted metal settled out over a period of 30 min with stirring discontinued. The supernatant brown solution was decanted into part B. The volatile materials (HSO_3F and $S_2O_6F_2$) were distilled back onto the unreacted metal by heating part B to 60 °C. Some more (~1 mL) $S_2O_6F_2$ was added at this point and the oxidation reaction was continued for another 24 h. The procedure was repeated four more times until all metal powder appeared to have been consumed. The dark brown solution in part B was heated to 140 °C for 12 more hours to ensure complete oxidation. At this stage the color of the solution changed to a deep blue-purple due to a decomposition of $Ir(SO_3F)_4$ to $Ir(SO_3F)_3$.[9] The solution was then transferred by decanting to reactor arm A for the carbonylation reaction.

All volatile materials (O_2, $S_2O_5F_2$, $S_2O_6F_2$, SiF_4, and HSO_3F) were removed *in vacuo* and about 3 mL of HSO_3F was added to produce a deep blue solution. At this stage CO gas (~2 atm) was admitted to the reactor and the solution was heated to 60 °C for about 4 days. The color of the solution changed gradually from blue to violet, then to brown, and to black. Finally a bright yellow solution resulted, and no color change was noted on further heating.

From the bright yellow solution, pale yellow, almost colorless crystals and a deep yellow solution were obtained after the removal of most volatiles. Recrystallization from HSO_3F produced single crystals suitable for an X-ray diffraction study. The total yield of crystalline material isolated and identified as *mer*-$Ir(CO)_3(SO_3F)_3$ was estimated to be ~70%.

Crystalline *mer*-$Ir(CO)_3(SO_3F)_3$ is an almost colorless, pale yellow material. Heating in a sealed capillary results in melting, gas evolution and a color change to light brown at 150 °C. Anal. Calcd for $C_3O_{12}F_3S_3Ir$: C, 6.28; S, 16.77; H, 0. Found: C, 5.7; S, 18.25; H, 0.1. No weight loss due to CO release is noted when the sample is kept *in vacuo* for several days.

(iv) X-ray Crystallography. Under a dry nitrogen atmosphere, a suitable fragment was cleaved from a colorless crystal and was gently wedged in a capillary tube with a trace of fluorocarbon grease as adhesive. The tube was hot-wire sealed in the glovebox. Data were recorded at 200 K with an Enraf Nonius CAD4F diffractometer equipped with an in-house modified low-temperature attachment using graphite monochromatized Mo K_α radiation. Intensity standards (two every hour) showed ±3% variations in intensity but no net decay. The data were corrected for the effects of absorption by the product of an empirical correction[10] and 2θ-dependent correction for a sphere of radius 0.1 mm. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

Table 1. Crystallographic Data for the Structure Determination of *mer*-$Ir(CO)_3(SO_3F)_3$ at 200 K

formula	$IrS_3F_3O_{12}C_3$	cryst syst	monoclinic
fw	573.42	space group	$P2_1/c$
a (Å)[a]	8.476(1)	ρ_c(g cm^{-3})	2.921
b (Å)	12.868(2)	λ(Mo Kα_1) (Å)	0.70930
c (Å)	12.588(1)	μ(Mo Kα) (cm^{-1})	107.6
β (deg)	108.24 (1)	min−max 2θ (deg)	4−50
V (Å)^3	1304.0	transm[b]	0.453−1.0
Z	4	cryst dimems (mm)	0.20 × 0.34 × 0.36
R_F[c]	0.022	R_{wF}[d]	0.024

[a] Cell dimensions were determined from 25 reflections ($38° \leq 2\theta \leq 50°$). [b] The data were corrected empirically for the effects of absorption. [c] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, for 2090 data ($I_o \geq 2.5\sigma(I_o)$). [d] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$ for 2090 data ($I_o \geq 2.5\sigma(I_o)$); $w = 1$.

The structure was solved from the Patterson map by the heavy atom method. The final full-matrix least squares refinement of 200 parameters, using 2090 data ($I_o \geq 2.5\sigma(I_o)$), included coordinates and anisotropical thermal parameters for all atoms and an extinction parameter.[11] The refinement converged at $R_F = 0.022$ and $R_{wF} = 0.024$, using unit weights.

The programs used for the structure determination were from the NRCVAX Crystal Structure System[12] and CRYSTALS.[13] Complex scattering factors for neutral atoms[14] were used in the calculation of structure factors. Computations were carried out on a MicroVAX-II and on 80486-processor-based personal computers. Crystallographic details are summarized in Table 1. Final fractional atomic coordinates are listed in Table 2.

The refined anisotropic atomic displacement parameters were analyzed in a manner analogous to that previously described for the structure of *cis*-$Pd(CO)_2(SO_3F)_2$[3,15,16] and yielded very similar results. The estimated ranges of corrections (always positive) to the bond lengths are given in the footnote to Table 3.

Results and Discussion

Like $Au(CO)SO_3F$[1] and *cis*-$M(CO)_2(SO_3F)_2$[2], M = Pd or Pt, tris(carbonyl)iridium(III) fluorosulfate, $Ir(CO)_3(SO_3F)_3$, is formed from a binary fluorosulfate precursor in fluorosulfuric acid by a reaction with gaseous CO according to:

$$Ir(SO_3F)_3 + 3CO \xrightarrow[4\ d,\ HSO_3F]{60\ °C,\ 2atm} Ir(CO)_3(SO_3F)_3 \qquad (1)$$

There are three important differences to the earlier formation reactions:

(i) The oxidation state of iridium remains +3 while $Au(CO)SO_3F$,[1] *cis*-$Pt(CO)_2(SO_3F)_2$,[2] or *cis*-$Pd(CO)_2(SO_3F)_2$[2]

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Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å)^2 for *mer*-$Ir(CO)_3(SO_3F)_3$ at 200 K

atom	x	y	z	U_{eq}[a]
Ir	0.27018(3)	0.590208(17)	0.255878(18)	0.0144
S(1)	0.30798(20)	0.82664(13)	0.19034(14)	0.0242
S(2)	−0.09454(18)	0.57702(13)	0.09385(13)	0.0225
S(3)	0.62836(19)	0.62602(13)	0.42295(13)	0.0224
F(1)	0.1271(5)	0.8666(3)	0.1515(3)	0.0358
F(2)	−0.1670(5)	0.6620(4)	0.1518(4)	0.0391
F(3)	0.5951(6)	0.7269(4)	0.4789(4)	0.0398
O(11)	0.3019(6)	0.7482(3)	0.2756(4)	0.0252
O(12)	0.3323(7)	0.7825(4)	0.0941(4)	0.0348
O(13)	0.4043(7)	0.9121(4)	0.2419(5)	0.0400
O(21)	0.0791(5)	0.6182(3)	0.1133(3)	0.0196
O(22)	−0.1852(6)	0.5833(4)	−0.0209(4)	0.0311
O(23)	−0.0968(6)	0.4857(5)	0.1541(5)	0.0388
O(31)	0.4632(5)	0.5711(3)	0.3994(3)	0.0206
O(32)	0.6633(6)	0.6577(4)	0.3252(4)	0.0312
O(33)	0.7489(6)	0.5721(4)	0.5075(4)	0.0325
O(1)	0.2278(6)	0.3563(4)	0.2543(4)	0.0303
O(2)	0.4756(6)	0.5740(4)	0.0899(4)	0.0275
O(3)	0.0458(6)	0.6191(5)	0.4071(4)	0.0364
C(1)	0.2427(7)	0.4407(5)	0.2527(5)	0.0225
C(2)	0.4074(7)	0.5804(5)	0.1522(5)	0.0223
C(3)	0.1283(8)	0.6057(5)	0.3553(5)	0.0232

[a] U_{eq} is the cube root of the product of the principal axes of the mean squared atomic displacement ellipsoid.

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for *mer*-$Ir(CO)_3(SO_3F)_3$ at 200 K

Bond Distances			
Ir-O(11)	2.055(4)[a]	S(2)-O(21)	1.511(4)[c]
Ir−O(21)	2.038(4)[a]	S(2)−O(22)	1.410(5)[g]
Ir−O(31)	2.038(4)[a]	S(2)−O(23)	1.402(6)[h]
Ir−C(1)	1.937(7)[b]	S(2)−F(2)	1.545(5)[i]
Ir−C(2)	2.006(6)[b]	S(3)−O(31)	1.512(4)[c]
Ir−C(3)	1.999(6)[b]	S(3)−O(32)	1.413(5)[j]
S(1)−O(11)	1.487(5)[c]	S(3)−O(33)	1.406(5)[k]
S(1)−O(12)	1.411(5)[d]	S(3)−F(3)	1.545(5)[l]
S(1)−O(13)	1.402(5)[e]	O(1)−C(1)	1.094(8)[m]
S(1)−F(1)	1.544(4)[f]	O(2)−C(2)	1.114(8)[n]
O(3)−C(3)	1.108(8)[o]		
Bond Angles			
O(11)−Ir−O(21)	88.25(17)	C(1)−Ir−C(2)	90.8(3)
O(11)−Ir−O(31)	88.49(17)	C(1)−Ir−C(3)	91.2(3)
O(11)−Ir−C(1)	174.41(23)	C(2)−Ir−C(3)	177.4(3)
O(11)−Ir−C(2)	93.46(23)	Ir−O(11)−S(1)	128.1(3)
O(11)−Ir−C(3)	84.67(23)	Ir−O(21)−S(2)	123.07(24)
O(21)−Ir−O(31)	176.74(17)	Ir−O(31)−S(3)	123.68(25)
O(21)−Ir−C(1)	95.74(22)	Ir−C(1)−O(1)	177.8(6)
O(21)−Ir−C(2)	84.30(20)	Ir−C(2)−O(2)	176.1(5)
O(21)−Ir−C(3)	93.79(21)	Ir−C(3)−O(3)	176.1(6)
O(31)−Ir−C(1)	87.52(22)		
O(31)−Ir−C(2)	95.80(20)		
O(31)−Ir−C(3)	86.00(21)		

[a−o] Thermal motion corrections using rigid body, segmented rigid body or riding models indicate that the actual bond lengths should be greater by from [a]0.003−0.008 Å; [b]0.003−0.004 Å; [c]0.003−0.011 Å; [d]0.009−0.013 Å; [e]0.011−0.020 Å; [f]0.014−0.016 Å; [g]0.010−0.010 Å; [h]0.014−0.022 Å; [i]0.019−0.024 Å; [j]0.009−0.010 Å; [k]0.009−0.016 Å; [l]0.015−0.020 Å; [m]0.005−0.018 Å; [n]0.003−0.010 Å; and [o]0.008−0.026 Å.

form in reductive carbonylation reactions[17] from $[Au(SO_3F)_3]_2$,[18] $Pt(SO_3F)_4$,[19] or $Pd^{II}Pd^{IV}(SO_3F)_6$,[20] respectively. The byproducts of the reduction, CO_2 and bis(fluorosulfuryl)oxide, $S_2O_5F_2$, are absent in the reaction described here.

(ii) Reductive carbonylation reactions in superacids are usually found to be very fast, and proceed easily at 25 °C within a few hours, particularly in the case of the reduction of the gold[1] and palladium[2] precursors. Formation of $Ir(CO)_3(SO_3F)_3$ is very slow and requires heating to 60 °C over 4 days. The reaction is easily followed by the color changes: the deep blue color of $Ir(SO_3F)_3$[9] dissolved in HSO_3F gradually changes to dark brown and finally to pale yellow-orange. While there is no precise structural information available for either solid $Ir(SO_3F)_3$ or its solution in HSO_3F, the observed weak temperature independent paramagnetism of the former[9] is consistent with a d^6 low spin configuration in an approximately octahedral environment. The compound is hence expected to be substitutionally inert.

(iii) Evidence from vibrational and ^{13}C-NMR spectra suggests that homoleptic metal carbonyl cations like linear $[Au(CO)_2]^+$ [1] and square planar $[M(CO)_4]^{2+}$ (M = Pt or Pd)[2] form initially in HSO_3F solution. All three cations have subsequently been obtained as $[Sb_2F_{11}]^-$ salts.[21,22] Substitution of CO by SO_3F^- in more concentrated solutions of the metal carbonyl cations in HSO_3F leads subsequently to $Au(CO)SO_3F$[1] and *cis*-$M(CO)_2(SO_3F)_2$[2], M = Pd or Pt. Consistent with the greater trans-directing ability of CO,[23a] the cis-isomers of $M(CO)_2(SO_3F)_2$, M = Pd or Pt, form exclusively.

There is so far no evidence in the vibrational and ^{13}C-NMR spectra for any homoleptic carbonyl cation of iridium as precursor in solution. Consequently the molecular structure and spectroscopic results, discussed below, point to the *mer*-isomer of $Ir(CO)_3(SO_3F)_3$ as the predominant form. Observation of a *trans*-$Ir(CO)_2$ moiety is consistent with the gradual, stepwise addition of CO to a fluorosulfate species, rather than with a substitution of CO by SO_3F^- as observed during the formation of $Au(CO)SO_3F$ from $[Au(CO)_2]^+$ [1] and $M(CO)_2(SO_3F)_2$ from $[M(CO)_4]^{2+}$ [2] with M = Pd or Pt. There is however, no conclusive evidence regarding the nature of solvated $Ir(SO_3F)_3$ in HSO_3F, to permit a more detailed discussion of the formation reaction of *mer*-$Ir(CO)_3(SO_3F)_3$.

It is noted that $Ir(CO)_3I_3$ is also formed by the CO addition to IrI_3 at 100 °C and 250 atm of CO.[5] For this compound two bands in the CO stretching region of the IR-spectrum have been reported, and this is consistent with a *fac*-isomer. The compound is apparently of low thermal stability and loses CO readily. $Ir(CO)_3F_3$, the other precedent for $Ir(CO)_3(SO_3F)_3$, is formed by fluorination of $Ir_4(CO)_{12}$ with a 6-fold excess of XeF_2 in HF at −40 °C.[4] ^{19}F- and ^{13}C-NMR spectra suggest initial formation of a mixture of *mer*- and *fac*-isomers. The pale yellow solid isolated from solution is the *fac*-isomer.[4] This is consistent with the presence of *fac*-$Ir(CO)_3$ moieties in the precursor $Ir_4(CO)_{12}$.

In the case of $Ir(CO)_3(SO_3F)_3$ the *mer*-isomer is formed predominantly. In addition *mer*-$Ir(CO)_3(SO_3F)_3$ is less soluble in HSO_3F than the *fac*-isomer. Slow evaporation produces crystals of *mer*-$Ir(CO)_3(SO_3F)_3$ which are isolated by removing the mother liquor by pipetting. The total yield is about 70%. The *mer*-geometry is retained on redissolution in HSO_3F as is evident from the ^{19}F-NMR spectrum, and isomerization in HSO_3F solution is not observed. The mother liquor has, after separation from the crystals, a measureable concentration of *fac*-

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$Ir(CO)_3(SO_3F)_3$, best detected by its vibrational spectrum. It is estimated that approximately 10−15% of the *fac*-isomer is formed.

While the carbonylation of iridium(III) fluorosulfate to give $Ir(CO)_3(SO_3F)_3$ is slow but straightforward, the synthesis of $Ir(SO_3F)_3$ by the oxidation of iridium metal with $S_2O_6F_2$ in HSO_3F is troublesome and time consuming for three main reasons.

(i) The system is chemically complex. At temperatures below 100 °C the reaction is very slow. At 130 °C the reaction proceeds to give dark brown $Ir(SO_3F)_4$, which then decomposes to blue $Ir(SO_3F)_3$, $S_2O_5F_2$, and O_2. $Ir(SO_3F)_3$ is then reoxidized and the reaction sequence constitutes a catalytic decomposition of $S_2O_6F_2$ into O_2 and $S_2O_5F_2$. At 160 °C the decomposition of $S_2O_6F_2$ becomes very rapid. In addition fluorosulfate radicals formed from $S_2O_6F_2$ are reported[23b] to produce O_2 and $S_2O_5F_2$ by reaction with the glass wall at ~120 °C. Hence the oxygen produced must be removed every 24 h in order to avoid an explosion, and a fresh portion of $S_2O_6F_2$ is added from time to time.[9] It is estimated that an about 20- to 40-fold excess of $S_2O_6F_2$ over the amount required by stoichiometry is needed, and the reaction takes several days to go to completion.[9]

(ii) At temperatures of ~140 °C, fluorosulfuric acid, which is used as a solvent will undergo self-dissociation according to:

$$HSO_3F \rightarrow SO_3 + HF \qquad (2)$$

This results in extensive glass attack and formation of SiF_4. It is thus not possible to follow the course of the reaction by weighing. We have in the past,[9] and here as well, not used metal reactors (Monel-A or nickel) to avoid contamination by other metal fluorosulfates.

(iii) The black-blue color of the product $Ir(SO_3F)_3$ makes it difficult to judge whether all of the metal has been consumed. In this study we have designed and used a reactor with a sidearm (see Figure 1), which permits decanting of the supernatant liquid after the remaining metal has settled to the bottom and subsequent condensation of the oxidizer and solvent back into the main reactor. In this manner pure $Ir(SO_3F)_3$ is eventually obtained in a relatively short period of time in order to reduce side reactions. To reduce the hazards, only small amounts of Ir (~100 mg) are used at a time.

In summary, the synthetic challenge in this study is not the preparation of $Ir(CO)_3(SO_3F)_3$ but rather the synthesis of the starting material $Ir(SO_3F)_3$ in sufficient quantities. Attempts to follow the original preparation[9] are not successful, because the recommended overall reaction time is far too long and the synthesis is now completely modified.

A final comment concerns the microanalytical results reported here. The difficulties in obtaining reasonable quantities of $Ir(SO_3F)_3$ and subsequently $It(CO)_3(SO_3F)_3$ discussed above have made it necessary to use very small quantities of material for product identification. The presence of very small amounts of hydrogen (about 0.1%) detected during microanalysis suggests that not all solvent (HSO_3F) has been removed from the sample used. If an approximate composition of $Ir(CO)_3(SO_3F)_3 \cdot 0.7\ HSO_3F$ is assumed the calculated values for C (5.5%), S (18.16%) and H (0.11%), agree very well with the found values of 5.7, 18.25, and 0.1% for C, S, and H, respectively. There is no evidence for the presence of HSO_3F in samples used for vibrational spectroscopy, which have been obtained in a different preparation.

Molecular Structure of *mer*-$Ir(CO)_3(SO_3F)_3$. The molecular structure, depicted in Figure 2, shows that the coordination about the iridium atom is octahedral with a meridional stereochemistry. The lengths of chemically equivalent bonds are not significantly different (see Table 3). Variations in chemically inequivalent Ir−C, Ir−O, and S−O(Ir) bond lengths are all consistent with the relative trans-influences[23a] of the ligands.

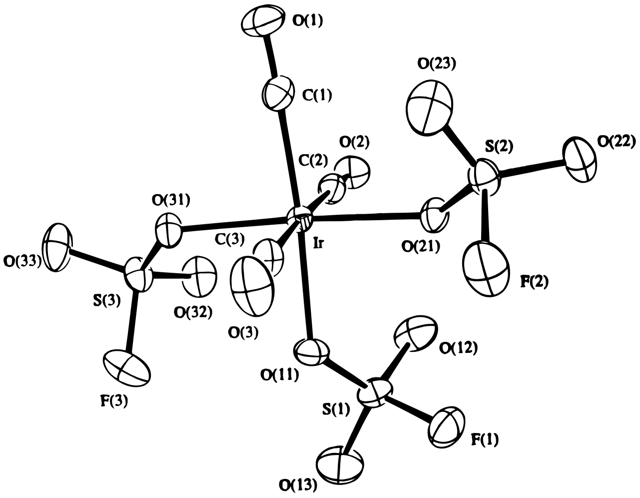

Figure 2. Molecular structure of *mer*-$Ir(CO)_3(SO_3F)_3$ at 200 K. The 50% probability atomic displacement ellipsoids are shown.

As expected from the spectroscopic results, the lengths of the C−O bonds lie at the lower end of the range exhibited by transition metal carbonyls.[24] The relatively large errors in the C−O bond lengths and uncertainties introduced by applying thermal motion corrections (Table 3) preclude more meaningful correlations with spectroscopic parameters.

As found for *cis*-$Pd(CO)_2(SO_3F)_2$[3] there are a number of intermolecular and unimposed intramolecular C−O contacts (three and one respectively for C(1), two of each for C(2) and one of each for C(3)) to terminal oxygen atoms of the fluorosulfate groups in the range 2.722(8)−3.069(8) Å. C(3) has in addition a weaker unimposed intramolecular contact with F(2) of 3.056(7) Å. The respective sums of accepted van der Waals radii are C + O = 3.22 Å and C + F = 3.17 Å.[25] These interactions are thought to be attractive in nature and to provide a stabilizing influence analogous to those in *cis*-$Pd(CO)_2(SO_3F)_2$. In the square planar palladium structure each carbon atom has five such contacts; however, the C−O distance ranges are somewhat longer (C−O range = 2.869(6)−3.172(6) Å and one C−F = 3.051(6) Å). This is a reasonable consequence of the lower coordination number and square planar geometry at Pd which would allow more secondary contacts to the CO groups from neighbouring molecules.

The extramolecular C−O interactions in the structure of *mer*-$Ir(CO)_3(SO_3F)_3$ link the molecules into an extended three-dimensional structure. There are also a few less severe non-bonded O--O contacts (in the range 2.917(7)−3.010(8) Å) and F−O contacts (2.880(7)−2.970(6) Å). These are marginally shorter than the respective sums of accepted van der Waals radii[25] (O + O = 3.04 Å and O + F = 2.99 Å respectively) and may be thought largely to be imposed as a result of the attractive C−O and C−F interactions. There are no further intermolecular separations significantly less than the sums of appropriate pairs of van der Waals radii.

Figure 3 depicts four complete molecules whose iridium atoms lie within a common unit cell plus additional atoms to show all the presumed attractive C-— and C−F contacts to one molecule, the atomic coordinates of which are given in Table 2.

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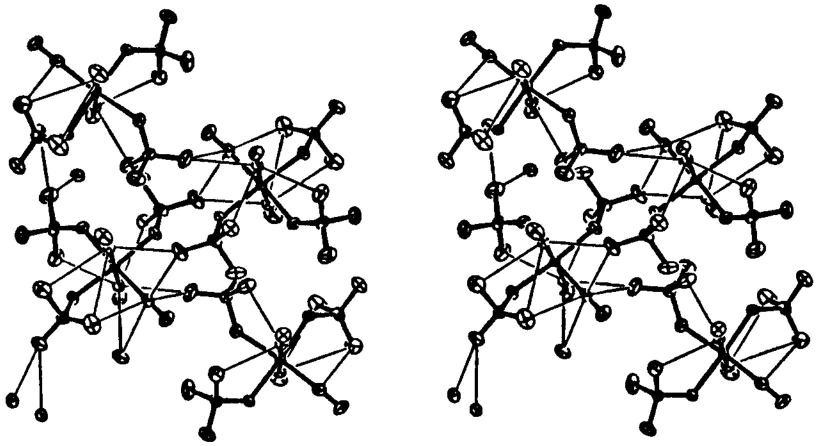

Figure 3. Stereoscopic view of four complete molecules of *mer*-$Ir(CO)_3(SO_3F)_3$ at 200 K, whose iridium atoms lie within a common unit cell, plus other symmetry related atoms (4 C and 1 O) sufficient to depict all attractive secondary interactions (thin lines) to one molecule (right, upper). The 50% probability atomic displacement ellipsoids are shown.

Table 4. Vibrational Data for *mer*-$Ir(CO)_3(SO_3F)_3$ and *cis*-$Pt(CO)_2(SO_3F)_2$[a]

mer-$Ir(CO)_3(SO_3F)_3$		*cis*-$Pt(CO)_2(SO_3F)_2$		
IR	Raman	IR	Raman	approx. assignment
2249 (w)	2249 (vs)	2219 (s)	2218 (vs)	$\nu(12CO)$
2208 (s)	2206 (w, sh)			$\nu(12CO)$
2198 (s)	2196 (s)	2185 (vs)	2181 (s)	$\nu(12CO)$
2168, 2150 (vw)				$\nu(13CO)$
1409 (s, sh)		1397 (s)	1395 (s)	
1394 (vs)	~1380 (m, sh)	1389 (s, sh)		$\nu_{asym}(SO_3)$
		1378 (vs)	1376 (m)	
		1362 (w, sh)		
		1230 (m, sh)		$\nu_{sym}(SO_3)$
1213 (vs)	1215 (s)	1209 (vs)	1212 (s)	
1030 (s)	1056 (m)	1034 (m, sh)		
1011 (s)	1024 (m)	1026 (s)	1019 (s)	$\nu SO\cdots M$
987 (vs)	1007	1009 (vs)	993 (m)	
932 (w, sh)				
829 (s)	825 (mw)	799 (s)	815 (w)	νSF
818 (s)	815 (mw)		792 (w)	
802 (s)				
658 (m, sh)		657 (ms)	656 (s)	$\nu(MO) + \delta(SO_2)$
643 (m, sh)	640 (s)	648 (m, sh)		
595 (s)	585 (m−w)	589 (s, sh)	588 (mw)	$\delta_{asym}(SO_3)$
		584 (s)	580 (m)	
548 (m, sh)	554 (m)	557 (ms)	565 (w)	$\delta_{sym}(SO_3)$
530 (s)	543 (m, sh)	551 (s)	554 (w)	
	512 (m)	476, 472 (ms)	475 (w, sh)	$\delta(M-CO)$?
451 (vs)	450 (ms)	436 (w)	462 (ms)	$\nu(MO) + \delta(SO_3)$
	403 (w)	411 (vw)	412 (w)	$\rho(SO_3F)$
	276 (s)		291 (m)	unassigned
			276 (vw)	torsion and
			175 (w)	def modes
			151 (m)	
	137 (s)		138 (vw)	

[a] Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, ν = stretching mode, sym = symmetric, asym = asymmetrical, δ = bonding mode, and ρ = rocking.

In spite of differences in stereochemistry and oxidation states of the two respective metals, the molecular structures of *mer*-$Ir(CO)_3(SO_3F)_3$ and of *cis*-$Pd(CO)_2(SO_3F)_2$ show very strong similarities in bond distances and angles for both the $M(CO)_n^-$ (M = Ir, Pd; n = 3 or 2) and the fluorosulfate moieties. Even the metal−oxygen distances are comparable for both compounds.

The iridium−carbon distances in the *trans*-$Ir(CO)_2$ group are, at 1.998(6) and 2.006(6) Å, identical within accuracy limits. Both are measurably longer than the third Ir−C distance of 1.937(6) Å due to the weak trans-influence of the fluorosulfate group. All three rank at the longer end of Ir−CO bonds to terminal CO groups, where for 148 examples a q_u value of 1.898 Å is quoted.[24] To account for the long iridium to carbon bonds strongly reduced Ir to CO π-back-donation, in particular in the *trans*-$Ir(CO)_2$ moiety, is suggested from the vibrational spectra which will be discussed next.

In summary, while the observed bond parameters with the possible exception of the short C−O and the long Ir−CO bond distances are not unusual, the molecular structure of *mer-Ir(CO)*$_3(SO_3F)_3$ is unique for three reasons: (i) *mer*-$Ir(CO)_3(SO_3F)_3$ is the first structurally characterized example of a metal carbonyl derivative of iridium(III) where π-back-donation is significantly reduced (vide infra); (ii) this is only the third case, after cis-$Pd(CO)_2(SO_3F)_2$[3] and $[Hg(CO)_2][Sb_2F_{11}]$,[26] where secondary contacts involving the electropositive C atoms of the

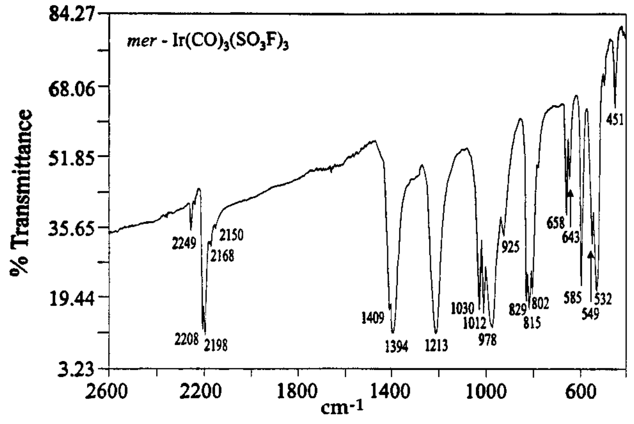

Figure 4. FT-IR spectrum of crystalline *mer*-Ir(CO)$_3$(SO$_3$F)$_3$.

carbonyl groups and the O or F atoms[3,26] of the SO$_3$F[3] groups or the [Sb$_2$F$_{11}$]$^-$ anion are observed;[26] (iii) with linear OC−M−OSO$_2$F configurations found for Au(CO)(SO$_3$F)[1] and *cis*-Pd(CO)$_2$(SO$_3$F)$_2$[3] the mer-geometry is unexpected and unusual. In addition the structure determination is of high accuracy, and thermal motion corrections are applied.

Vibrational Spectra. The FT-IR and FT-Raman band positions observed for crystalline *mer*-Ir(CO)$_3$(SO$_3$F)$_3$ are listed in Table 4 together with estimated intensities, the corresponding vibrational data for *cis*-Pt(CO)$_2$(SO$_3$F)$_2$, which are very similar to those of *cis*-Pd(CO)$_2$(SO$_3$F)$_2$[2], and an approximate assignment of the bands.

The FT-IR spectrum of *mer*-Ir(CO)$_3$(SO$_3$F)$_3$ is shown in Figure 4. In Figure 5 we compare the CO-stretching regions in the Raman spectrum of crystalline *mer*-Ir(CO)$_3$(SO$_3$F)$_3$ to the solution Raman spectrum of the mother liquor, removed from the crystals by pipetting.

Except for some more extensive band splitting for *mer*-Ir(CO)$_3$(SO$_3$F)$_3$, particularly in the 1000−800 cm^{-1} region (assigned to ν(SO···M) and ν(SF), the vibrational spectra for both compounds in the SO$_3$F region are identical. Some small variations in band positions in the 400−512 cm^{-1} range are consistent with our proposed assignment[2] of these bands as being due to the metal carbonyl moieties of both compounds. While Ir(CO)$_3$ bands in the 400−500 cm^{-1} region are difficult to assign and in some cases even more difficult to detect, a clear picture is presented in the CO stretching frequency region. For *mer*-Ir(CO)$_3$(SO$_3$F)$_3$ three CO stretching modes are expected and observed even though the band at 2206 cm^{-1}, (assigned to a B$_2$ mode) is poorly resolved in the Raman spectrum, while both A$_1$ modes at 2249 and 2196 cm^{-1} respectively are very intense. Alternately the 2249 cm^{-1} band is weak in the IR spectrum. This would suggest a $\bar{\nu}_{av}$(CO) value of 2218 cm^{-1}, about 75 wavenumbers higher than found for gaseous CO (2143 cm^{-1}).[27] A stretching force constant, f_r of (19.9 ± 0.1) × 10^2 N m^{-1} is obtained using the two mass model. We had previously reported a f_r value of 19.5 × 10^2 N m^{-1} [21] for Au(CO)SO$_3$F with $\bar{\nu}$(CO) at 2196 cm^{-1} while for *cis*-Pt(CO)$_2$(SO$_3$F)$_2$ $\bar{\nu}_{av}$ = 2202 cm^{-1} and f_r is (19.6 ± 0.1) × 10^2 N m^{-1}. Hence it appears that for the noble metal carbonyl fluorosulfates in the 5d-block the strength of the CO bond gradually increases with increasing formal charge of the metal. This in turn suggests gradually decreasing π-back-donation as we progress from Au(CO)SO$_3$F through *cis*-Pt(CO)$_2$(SO$_3$F)$_2$ to *mer*-Ir(CO)$_3$(SO$_3$F)$_3$. If the two bands at 2249 and 2208 cm^{-1} are attributed to the *trans*-Ir(CO)$_2$ moiety and $\bar{\nu}$(CO) at 2198 cm^{-1} to CO trans to SO$_3$F, two stretching force constants, f_r, of 20.0 × 10^2 and 19.5 × 10^2 N m^{-1} are obtained.

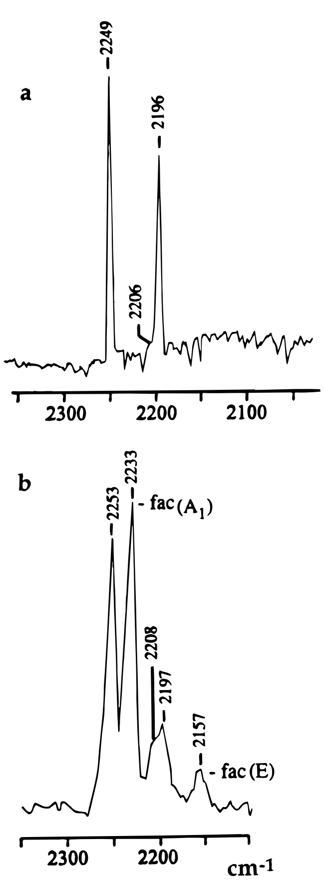

Figure 5. FT-Raman spectrum in the CO-stretching range of (a) crystalline *mer*-Ir(CO)$_3$(SO$_3$F)$_3$ and (b) a mixture of *mer*- and *fac*-Ir(CO)$_3$(SO$_3$F)$_3$ dissolved in HSO$_3$F.

There are reports of vibrational studies of iridium(III) carbonyl derivatives[27] and for complexes of the type IrCl$_3$(CO)(PR$_3$)$_2$, R = C$_2$H$_5$ or n-C$_4$H$_9$, $\bar{\nu}$(CO) is found between 2010 and 2090 cm^{-1}.[28] It appears that the phosphine ligands are better σ-donors than CO which in turn results in enhanced π-back-donation to CO and $\bar{\nu}$(CO) will now fall in the expected range for terminal CO ligands.[29a] We have made similar observations recently for various palladium(I) carbonyl complexes with other π-acid ligands.[29b]

As can be seen in Figure 4, two additional $\bar{\nu}$(CO) stretching modes are observed in the Raman spectrum of the mother liquor in HSO$_3$F solution. The two bands at 2233 (A$_1$) and 2157 (E) cm^{-1} with IR counterparts at 2232 (A$_1$) and 2156 (E) cm^{-1} are assigned, based on band intensities, to the *fac*-Ir(CO)$_3$(SO$_3$F)$_3$. These band positions correspond well to $\bar{\nu}$(CO) reported for *fac*-Ir(CO)$_3$F$_3$[4] at 2213 and 2165 cm^{-1}. The average $\bar{\nu}$(CO) values for *fac*-Ir(CO)$_3$(SO$_3$F)$_3$ and *fac*-Ir(CO)$_3$F$_3$ of 2183 and 2181 cm^{-1} respectively suggest CO bonds of comparable strength and a stretching force constant of (19.2 ± 0.1) × 10^2 N m^{-1} is obtained. Finally for Ir(CO)$_3$I$_3$,[5] assuming facial symmetry and identical irreducible representations for the two reported bands $\bar{\nu}_{av}$(CO) is 2135 cm^{-1} and f_r is 18.4 × 10^2 N m^{-1}, slightly lower than for gaseous CO (18.6 × 10^2 N m^{-1}).

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When *mer*-$Ir(CO)_3(SO_3F)_3$ is redissolved in HSO_3F two Raman bands at 2253 and 2197 cm^{-1} are found, the latter with a poorly resolved shoulder at ~2205 cm^{-1}. It appears that isomerization in solution does not occur or does not occur rapidly. For the same solution two ^{19}F-NMR resonances due to the solute are observed at 43.35 and 43.57 ppm of an approximate peak area ratio of 1:2.

There is an alternative interpretation for the two bands at 2233 and 2157 cm^{-1} which are also observed in polycrystalline samples. Both bands could be due to $Ir(CO)_2(SO_3F)_3$, which is a possible precursor in the formation of $Ir(CO)_3(SO_3F)_3$ during gradual CO addition. Since bands attributable to either bridging SO_3F groups or bridging CO are not observed, the precursor would have to be a monomer. The coincidence of IR and Raman bands would then suggest *cis*-$Ir(CO)_2(SO_3F)_3$ as the sole isomer, rather than an isomer mixture reflecting the trans-directing ability of CO. Furthermore the broadness and low Raman intensity of the band 2157 cm^{-1} is more consistent with an E-mode in *fac*-$Ir(CO)_3(SO_3F)_3$ than an A′ mode of *cis*-$Ir(CO)_2(SO_3F)_3$.

Thus it appears that CO bonding is slightly stronger in *mer*-$Ir(CO)_3(SO_3F)_3$ than in the *fac*-isomer. We have commented in the preceding section on the difference in Ir−C bond length due to the trans-influence exerted by the fluorosulfate group. It may be argued that in the *trans*-$Ir(CO)_2$-moiety there is more competition for π-electron density from the metal while oxygen of the fluorosulfate group functions as a weak π-donor toward the iridium(III) center.

In compounds of the type $IrCl_3(CO)(PR_3)_2$,[28,29a] $R = CH_3$ or C_4H_9, where several geometrical isomers have been obtained and studied by IR in $CHCl_3$ as solvent, $\bar{\nu}(CO)$ is always higher by 30−40 wavenumbers when the CO group is trans to phosphine compared to trans to chlorine. The CO stretching frequencies for these compounds are observed in the region between 2050 and 2100 cm^{-1}.

It is tempting to postulate the complete absence of π-back-bonding in compounds with $\bar{\nu}(CO)$ above 2200 cm^{-1}.[29,30] It is our view[30,31] that there still is residual π-back-donation, as long as the stretching force constant f_r stays below 21.3×10^2 N m^{-1}, the value for HCO^+.[2] The closest approach to a "no π-back-bonding" situation is found for the $[Hg(CO)_2]^{2+}$ cation, reported by us recently,[26] where f_r is $21.0 + 0.1 \times 10^2$ N m^{-1}. All other f_r values reported here or elsewhere fall short.

The iridium(III) carbonyl derivatives discussed here[4,5,28,29] clearly show, as phosphines or other π-acid ligands are replaced by CO to give tris(carbonyl)−Ir(III) derivatives and as the anionic ligands become harder and more electron withdrawing, that metal CO bonding changes. π-back-donation decreases gradually as $\bar{\nu}(CO)$ increases to values well above 2143 cm^{-1}, and the $\bar{\nu}$ value of free CO[25] and σ-bonding becomes predominant.

Summary and Conclusions

With the synthesis of *mer*-$Ir(CO)_3(SO_3F)_3$ by CO addition to $Ir(SO_3F)_3$[9] and its characterization by vibrational spectroscopy and single-crystal X-ray diffraction described here, the range of cationic metal carbonyls with significantly reduced π-back-bonding is for the first time expanded from groups 11 (Ag(I) and Au(I)) and 10 (Pd(II) and Pt(II)) to iridium(III) in group 9. The sharp reduction in π-back-donation is evident from the long Ir−C bonds, $\bar{\nu}_{av}(CO)$ of 2218 cm^{-1}, and the stretching force constant f_r of 19.9 x 10^2 N m^{-1}.

Iridium is hence found to form cationic, uncharged[32] and with $[Ir(CO)_3]^{3-}$ [33] also highly reduced carbonyl derivatives. As the oxidation state of the metal ranges from +3 to −3, $\bar{\nu}(CO)$ values for terminal CO ligands range from a high of 2249 cm^{-1} for the A_1 mode in *mer*-$Ir(CO)_3(SO_3F)_3$ to a low of 1642 cm^{-1} for the $[Ir(CO)_3]^{3-}$ anion.[33]

As observed previously for *cis*-$Pd(CO)_2(SO_3F)_2$[3] significant inter- and intramolecular SO−CO contacts appear to exert a stabilizing influence on the structure of *mer*-$Ir(CO)_3(SO_3F)_3$. In addition bond parameters, such as bond lengths and bond angles, for *mer*-$Ir(CO)_3(SO_3F)_3$ and *cis*-$Pd(CO)_2(SO_3F)_2$[3] compare well, when the trans influence of CO and SO_3F respectively are taken into account. The only apparent difference between both metal carbonyl fluorosulfates is the stereochemistry, which is cis for $Pd(CO)_2(SO_3F)_2$ and *mer* (or trans) for $Ir(CO)_3(SO_3F)_3$. This appears to be a consequence of the formation reaction: *cis*-$Pd(CO)_2(SO_3F)_2$ forms when two CO ligands in square planar $[Pd(CO)_4]^{2+}$ are replaced by two SO_3F^- ions, while in solvated $Ir(SO_3F)_3$ gradual addition of CO takes place. The resulting geometries are hence in both cases a consequence of the strong trans-directing ability of the CO group.

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Supporting Information Available: Tables of supplementary crystallographic data, anisotropic displacement parameters, selected intramolecular torsion angles, distances, and angles, and unique intermolecular and unimposed intramolecular secondary interaction contact distances (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information. For access on the World Wide Web for journal subscribers (http://pubs.acs.org), files are presented in Crystallographic Information Format (CIF).

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