Hexakis(carbonyl)iron(II) Undecafluorodiantimonate(V), [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$, and -Hexafluoroantimonate(V), [Fe(CO)$_6$][SbF$_6$]$_2$, Their Syntheses, and Spectroscopic and Structural Characterization by Single Crystal X-ray Diffraction and Normal Coordinate Analysis

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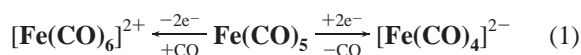
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Abstract: Hexakis(carbonyl)iron(II) undecafluorodiantimonate(V), [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$, is conveniently prepared by the oxidative carbonylation of Fe(CO)$_5$ with XeF$_2$ as external oxidizer in the conjugate Brønsted-Lewis superacid HF−SbF$_5$. The colorless compound crystallizes from the reaction medium in high purity. The molecular structure is obtained by single-crystal X-ray diffraction. The cation is a regular octahedron, while the vertex-shared di-octahedral [Sb$_2$F$_{11}$]$^-$ anion is distorted from D_{4h} symmetry by bending and rotational processes, due to significant interionic interactions, primarily of the F···C type. Washing of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ with anhydrous HF results in an unusual elution of SbF$_5$ and the quantitative conversion to hexakis(carbonyl)-iron(II) hexafluoroantimonate(V) [Fe(CO)$_6$][SbF$_6$]$_2$. The molecular structure of the salt shows octahedral ions with slight tetragonal distortions for the cation (elongation) and the anion (compression). Both salts are thermally stable up to 150 °C. The averaged bond distances and the vibrational wavenumbers of [Fe(CO)$_6$]$^{2+}$ are nearly identical in both compounds. The [Fe(CO)$_6$]$^{2+}$ cation, the first and so far only isolated and structurally characterized dipositive, superelectrophilic carbonyl cation formed by a 3d-metal, is further characterized by a normal coordinate analysis (NCA). The obtained force constants are compared to those of the isoelectronic molecule Cr(CO)$_6$. Changes in π-back-bonding affect the $F_{CO/CO}$ and $F_{CO/MC}$ interaction force constants more strongly than the stretching force constants F_{CO} and F_{MC}. All 13 fundamentals of [Fe(CO)$_6$]$^{2+}$ are detected and assigned with the help of the data obtained from the normal coordinate analysis and density functional calculations published previously. The electronic ground state $^1A_{1g}$ of the [Fe(CO)$_6$]$^{2+}$ cation is established by magnetic susceptibility measurements of polycrystalline [Fe(CO)$_6$][SbF$_6$]$_2$ and [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ between 2 and 300 K. The magnetic impurity formed during synthesis is identified as Fe[SbF$_6$]$_2$ which has iron(II) in high spin ($^5T_{2g}$) ground state. Consistent with a diamagnetic ground state are the single line in the ^{57}Fe Mössbauer spectrum (i.s. = −0.003(8) mm s^{-1} relative to α-Fe), obtained on polycrystalline samples and the single sharp line in the ^{13}C NMR spectrum in DF solution at 178 ppm with J (^{57}Fe-^{13}C) of 19.2 Hz.

Introduction

Iron forms three homoleptic, mononuclear 18-electron carbonyl species,[1−3] which are formally connected by 2-electron reduction−oxidation and CO-addition−elimination reactions as illustrated below:

$$[\mathbf{Fe(CO)_6}]^{2+} \underset{+CO}{\overset{-2e^-}{\rightleftarrows}} \mathbf{Fe(CO)_5} \underset{-CO}{\overset{+2e^-}{\rightleftarrows}} [\mathbf{Fe(CO)_4}]^{2-} \quad (1)$$

They represent with octahedral, trigonal bipyramidal, and tetrahedral geometries the three most common coordination polyhedra in metal carbonyl chemistry.[1−3] In the absence of any highly reduced iron carbonylates,[4] the three species have remained the only thermodynamically stable, mononuclear, homoleptic iron carbonyl complexes. The oxidation state of Fe ranges from +2 to −2. The history of their discoveries spans more than a century.

The oldest member of the triad, Fe(CO)$_5$, was first reported in 1891 by Mond, Langer, and Quincke.[5] Its synthesis followed

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one year after the accidental discovery of $Ni(CO)_4$ by the same authors.[6] Since that time, $Fe(CO)_5$ has been found to have a rich chemistry[1-3,7] with many industrial applications. The readily obtainable $Fe(CO)_5$ [1-3] provides a convenient starting material for the generation of salts with either $[Fe(CO)_4]^{2-}$ or $[Fe(CO)_6]^{2+}$ as constituent ions, as will be discussed below.

The anion $[Fe(CO)_4]^{2-}$ appears to have been first obtained in 1929 by Hock and Stuhlmann[8] as reported two years later. Subsequent reports[9,10] establish the reductive degradation of $Fe(CO)_5$ in aqueous alkaline solution as a convenient route to $[Fe(CO)_4]^{2-}$. The reduction of $Fe(CO)_5$ by alkaline metals in liquid ammonia[11] has provided subsequently a convenient alternative. One of the alkali metal salts, $Na_2[Fe(CO)_4]$, is known as "Collman's reagent".[2,3] It finds extensive use as a "super nucleophile" in organic chemistry for a wide range of oxidative addition reactions.[1-3,12]

The existence of the cation $[Fe(CO)_6]^{2+}$ has long been anticipated.[13,14] However, early claims of its formation in a halide abstraction reaction from $Fe(CO)_4X_2$, X = Cl, Br, by AlX_3 at high temperatures and CO pressures[15] had to be retracted.[16] Nevertheless the synthetic approach used has produced the salts $[M(CO)_6][AlX_4]$, M = Mn, Tc, Re, X = Br, with the first homoleptic metal carbonyl cations.[17-19] Equally erroneous has been the reported formation of $[Fe(CO)_6]^{2+}$ during the amine-catalyzed disproportionation of $Fe(CO)_5$.[20] Thus even though related cations of the type $[Fe(CO)_5X]^+$, X = Cl, Br, NO, H, are known,[21] $[Fe(CO)_6]^{2+}$ as well as other multiply charged or "super electrophilic"[22] homoleptic metal carbonyl cations has remained elusive until recently.

A new synthetic methodology and the extensive use of superacids[23,24] as reaction media, recently reviewed by Weber[25a] and two of us,[25b] has allowed the generation of a wide range of homoleptic carbonyl cations of metals in the groups 8-12, among them $[Fe(CO)_6]^{2+}$. Of the superacidic media the Lewis superacid SbF_5[23,24] has found exclusive use and the superacid anion $[Sb_2F_{11}]^-$,[26] formed by self-assembly in liquid SbF_5, has permitted the isolation of thermally stable salts.[25b]

Initial attempts by us to synthesize salts with octahedral $[M(CO)_6]^{2+}$, M = Fe, Ru, Os, cations have only been partly successful. The reductive carbonylations of MX_3, M = Fe, Ru, Os and X = Cl or SO_3F, in liquid SbF_5 have succeeded for ruthenium and osmium, where $[M(CO)_6][Sb_2F_{11}]_2$,[27] M = Ru, Os, form cleanly and in quantitative yield. When either $FeCl_3$ or $Fe(SO_3F)_3$ is used as a starting material, the previously known compound $Fe[SbF_6]_2$[28] forms in quantitative yield. The oxidative carbonylation of $Fe(CO)_5$ in liquid SbF_5 with either AsF_5 or Cl_2 as external oxidizing agents produces $[Fe(CO)_6][Sb_2F_{11}]_2$.[29] However, as will be discussed below, neither method is capable of giving either pure or crystalline material suitable for a complete characterization. We have subsequently developed a new synthetic approach where the Lewis superacid SbF_5 is replaced by the conjugate superacid $HF-SbF_5$[23,24] as reaction medium. In addition, in the oxidative carbonylation of $Fe(CO)_5$, xenon difluoride is used as oxidizing agent.

As a consequence $[Fe(CO)_6][Sb_2F_{11}]_2$ is obtained in high yield and in the form of single crystals. This permits a molecular structure determination by X-ray diffraction. The use of anhydrous hydrogen fluoride as solvent allows the facile conversion to $[Fe(CO)_6][SbF_6]_2$ according to the following:

$$[Fe(CO)_6][Sb_2F_{11}]_2 + 2HF \xrightarrow{\text{anh HF}}$$
$$[Fe(CO)_6][SbF_6]_2 + 2(HF \cdot SbF_5) \quad (2)$$
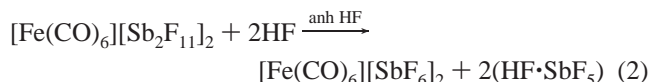
After repeated washings with HF, $[Fe(CO)_6][SbF_6]_2$ is formed as single crystals and its molecular structure is readily obtained.

The stabilization of $[Fe(CO)_6]^{2+}$ by two different counteranions, $[Sb_2F_{11}]^-$ and $[SbF_6]^-$, the latter an octahedral species with a simple vibrational spectrum, permits a complete vibrational analysis of the cation, including a normal coordinate analysis (NCA), assisted by recent ab initio calculations.[30,31] Comparisons are possible with isoelectronic $Cr(CO)_6$[32,33] and $[Mn(CO)_6]^+$.[34] For $[Re(CO)_6]^+$ the molecular structure[35,36] and a detailed vibrational study[37] are reported. There are also recent theoretical calculations on hypothetical gaseous $[M(CO)_6]_g^{n+}$, n = 1, 2, or 3 species.[31,38,39]

The high purity, in which both $[Fe(CO)_6]^{2+}$ salts are obtained, allows temperature-dependent magnetic susceptibility measurements, ^{57}Fe Mössbauer studies, and the recording of a UV-vis spectrum, which in turn permits a comparison to related precedents.[40] Finally a comparison of structural and spectroscopic parameters for the other two mononuclear iron carbonyl species $Fe(CO)_5$[41-44] and $[Fe(CO)_4]^{2-}$[45] to those of $[Fe(CO)_6]^{2+}$ will be undertaken.

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In summary a detailed and comprehensive study of [Fe-$(CO)_6]^{2+}$ is presented here, which extends from the development of a new synthetic approach, the structure determination with both $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ as counterions to the extensive spectroscopic characterization, including a normal coordinate analysis.

Experimental Section

General Procedures and Reagents. (a) Apparatus. Volatile materials were manipulated in a glass or stainless steel vacuum line of known volume equipped with a capacitance pressure gauge (Type 280E, Setra Instruments, Acton, MA) and valves with PTFE stems (Young, London) or stainless steel needle valves (3762H46Y Hoke, Creskill, NJ), respectively. Anhydrous HF or DF, both containing a few percent of SbF_5, were stored in PFA tubes (12 mm o.d., 300 mm long), heat gun sealed at the bottom, and connected on top to a stainless steel needle valve (3762H46Y Hoke, Cresskill, NJ). All other volatile compounds were stored in glass containers equipped with a valve with PTFE stem (Young, London). In the case of ^{13}CO, the storage vessel contained a molecular sieve (5 Å, Merck) to recover the excess of ^{13}CO after use by cooling with liquid nitrogen. For synthetic reactions in HF/SbF_5 solutions a reactor was used consisting of a 120 mL PFA bulb with a NS 29 socket standard taper (Bohlender, Lauda, Germany) in connection with a stainless steel NS 29 cone standard taper and a needle valve (3762H46Y Hoke, Cresskill, NJ). Both parts were pressed together with a metal flange and the reactor was leak tight ($<10^{-5}$ mbar L s^{-1}) without using grease. A two part V-shaped PFA vessel with valve was used for washing the product with anhydrous HF. Solid materials were manipulated inside an inert atmosphere box (Braun, Munich, Germany) filled with argon, with a residual moisture content of less than 0.1 ppm. In an evacuable box (Mecaplex, Grenchen, Switzerland) filled with dry nitrogen, supernatant HF/SbF_5 solutions over crystalline products were pipetted off the reactor.

(b) Chemicals. Anhydrous HF (Solvay, AG Hannover, Germany), SbF_5 (Elf Atochem, North America), $Fe(CO)_5$ (purity not stated, BASF Ludwigshafen, Germany), CO (99%, Linde Gas), and ^{13}CO (99% enriched, IC Chemicals) were obtained from commercial sources. Fe-$(CO)_5$ and SbF_5 were purified by trap-to-trap distillation and CO by condensation at -196 °C followed by partial re-evaporation. DF was prepared from D_2O (99.9%, Merck) and an excess of IF_5 (J. T. Baker Chemical Co.) followed by trap-to-trap distillation. XeF_2 was obtained by the photolysis of equimolar mixtures of Xe (Messer Griesheim, Düsseldorf, Germany) and F_2 (Solvay AG, Hannover, Germany) according to a literature procedure.[46] $Fe(^{13}CO)_5$ was synthesized by repeated CO-exchange between $Fe(CO)_5$ and ^{13}CO in $THF/NaBH_4$ suspension following a published procedure.[47] From the volatile THF/$Fe(^{13}CO)_5$ product mixture, THF was separated by trap-to-trap distillation and selective absorption of THF on $AlCl_3$ at room temperature. The ^{13}C content of the final product (50% yield) was about 95%. Fe-$[SbF_6]_2$ was prepared by the oxidation of iron powder by SbF_5 in SO_2 as described previously.[48]

(c) Instrumentation. (1) Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on a IFS-66v FT spectrometer (Bruker, Karlsruhe, Germany). Two different detectors together with a Ge/KBr or a 6 μm Mylar beam splitter operating in the region 5000–400 or 550–80 cm^{-1}, respectively, were used. One-hundred twenty-eight scans were co-added for each spectrum, using an apodized resolution of 2 or 4 cm^{-1}. The samples were crushed between CaF_2, AgBr (Korth, Kiel, Germany), or polyethylene (Cadillac, Hannover, Germany) disks inside the drybox. Raman spectra were recorded at

room temperature with a Bruker FRA-106 FT Raman accessory mounted on an optical bench of the IFS-66v instrument using the 1064 nm exciting line ($\sim$500 mW) of a Nd:YAG laser (Adlas, DPY 301, Lübeck, Germany). Crystalline samples were contained in large melting point capillaries (∅ 2 mm) for recording spectra in the region 5000–80 cm^{-1} with a spectral resolution of 2 cm^{-1}.

(2) NMR Spectroscopy. ^{13}C NMR spectra were obtained at room temperature on a Bruker MSL-200 FT spectrometer operating at 50.330 MHz. A 4 mm (o.d.) PFA tube containing a saturated HF solution (with a few percent SbF_5) over solid [Fe($^{13}CO)_6$][Sb_2F_{11}]_2 was centered inside a 10 mm glass NMR tube containing the lock and external reference $CDCl_3$ ($\delta = 77.7$ ppm referenced to TMS). With this sample it was possible to determine the chemical shift of [Fe($^{13}CO)_6]^{2+}_{solv}$ and to estimate a solubility of 5 mmol L^{-1} by comparing the signal intensity with the signal of $^{13}CDCl_3$ in natural abundance. However, even after 1 day of acquisition time, the S/N ratio was too low for detection of the ^{57}Fe satellites. For this purpose a saturated [Fe($^{13}CO)_6$][Sb_2F_{11}]_2 solution in deuterium fluoride, DF (containing a few percent SbF_5), was investigated in a 9 mm (o.d.) PFA tube placed in a 10 mm (o.d.) glass NMR tube. Measurement parameters: pulse length 3 μs, time between pulses 14 s, resolution 0.04 Hz/datapoint.

(3) UV Spectroscopy. UV–Vis spectra were recorded in the region 200–500 nm with a 1024 Diode Array spectrometer system (Spectroscopy International) using a CLD 30-W deuterium lamp (Hamamatsu, Japan) as light source. Hg emission lines were used for wavelength calibration. Single crystals of [Fe($^{13}CO)_6$][Sb_2F_{11}]_2 of suitable sizes were placed in an evacuable dry quartz cell of 1 mm optical path length (Hellma, Mülheim, Germany). To reduce scattering losses of light from the surface of the crystals, we added SbF_5 to the cell in vacuo. In front of the entrance slit of the monochromator, the crystals, immersed in SbF_5, were illuminated by the deuterium lamp via a quartz lens and a suitable aperture. The reference spectrum was measured with the same cell and aperture at a spot without any crystals.

(4) Mössbauer Spectroscopy. The ^{57}Fe Mössbauer spectrum of [Fe-$(CO)_6$][SbF_6]_2 was recorded using a ^{57}Co in rhodium source (Amersham-Buchler UK) with constant acceleration mode. Details about the apparatus are given elsewhere.[49] A polycrystalline sample (137 mg) was distributed over an area of about 1 cm^2 in an airtight polyethylene container. The spectrum was measured at 80 K sample temperature within several hours, and the isomer shift δ is referenced to α-Fe at room temperature.

(5) Magnetic Susceptibility Measurements. Magnetic susceptibility measurements of [Fe(CO)_6][SbF_6]_2 were performed in the temperature range 2–400 K using SQUID systems (MPMS 7, or MPMS R2 Quantum Design) with a one Tesla superconducting magnet. Polycrystalline samples weighing 40–220 mg were placed either in a quartz tube (5 mm o.d., 100 mm long) flame sealed under vacuum or in a PVC container. After the experiment a similar empty container was measured under the same conditions.

(6) X-ray Diffraction. Under dry argon atmosphere, fragments from single crystals of [Fe(CO)_6][Sb_2F_{11}]_2 and [Fe(CO)_6][SbF_6]_2 were cleaved and gently wedged in 0.3 mm capillary tubes with a trace of fluorocarbon grease as an adhesive. Data were recorded at room temperature with a Stoe IPDS-diffractometer using graphite monochromatized Mo Kα radiation. The systematic absences observed for X-ray data of [Fe(CO)_6][Sb_2F_{11}]_2 uniquely define the probable monoclinic space group to be $P2_{1/n}$, and those for [Fe(CO)_6][SbF_6]_2 point to two probable space groups $P4nc$ and Pr/mnc, of which the latter centrosymmetric one was chosen on the basis of the successful crystal structure determination. The structures were solved in $P2_1/n$ or Pr/mnc, respectively, by direct methods (SHELXS-86),[50] and the final full-matrix least squares refinements of all atomic parameters (SHELXL-93)[51] were carried out on a DECα Vax computer. The figures were drawn using the DIAMOND program.[52]

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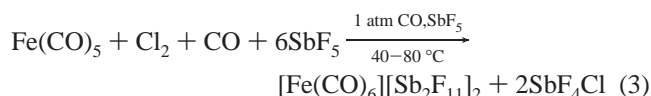(50) Sheldrick, G. M. SHELXS-86, Program for crystal structure solution, Universität Göttingen, 1986.

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(d) Synthetic Reactions. (1) The synthesis of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$. The PFA reactor described above, containing a PTFE coated magnetic stirring bar, was charged with 0.57 g (3.4 mmol) of XeF$_2$, 7 mL (97 mmol) of SbF$_5$, and 5 mL (250 mmol) of HF using a stainless steel vacuum line. The mixture was stirred at room temperature to give a homogeneous solution. At −196 °C, 0.47 g (2.4 mmol) of Fe(CO)$_5$ and 6 mmol of CO were admitted to the reactor. By use of an ethanol cold bath, the content was stirred at −50 °C for 10 min. During this time the color of the suspension changed from yellow to orange. After warming to 0 °C the solution became homogeneous. Subsequently the content was heated to 50 °C for 2 days without stirring and colorless single crystals of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ several millimeters in length were formed. In the evacuable drybox the liquid phase was pipetted off and the crystals were transferred into a V-shaped reactor. The crystalline product was washed with a SbF$_5$/HF (v/v 1:1) mixture. After removal of all volatiles in vacuo, 1.35 g (1.2 mmol) of pure [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ was obtained (50% yield). [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ is a colorless moisture-sensitive crystalline solid which is thermally stable to 150°. Heating beyond this point resulted in the formation of a colorless viscous liquid, identified as SbF$_5$, before evolution of CO was observed on further heating. Band positions and intensities attributed to the [Sb$_2$F$_{11}$]$^-$ anion in [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ and [Fe(^{13}CO)$_6$][Sb$_2$F$_{11}$]$_2$ are the following: IR, νSbF, 723 (w,sh), 712(w,sh), 692(vs), 670(w,sh), 657(vs), 599(w), 492-(vs); 2δSbF, 430(vw), δSbF; 336(s), 303(s), 277(s), 232(s), 203(w,-sh), and 127(w); Raman, νSbF, 709.2(w), 694.5(m), 686.8(m), 670.5(s), 647.9(s), 601(vw,sh), 598.1(m), 591.3(w,sh), δSbF; 332.6(vw), 299.3-(m), 275.5(w), 235.6(w), 226.6(w), and 207.4(vw). The isotopomer [Fe-(^{13}CO)$_6$][Sb$_2$F$_{11}$]$_2$ is synthesized in an identical manner by using enriched Fe(^{13}CO)$_5$ (see ref 47) and ^{13}CO. The ^{13}C contents of the product were judged to be 95%.

(2) Synthesis of [Fe(CO)$_6$][SbF$_6$]$_2$. To 1.012 g of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ contained in a "inverted V" reactor made from PFA was condensed 2 mL of anhydrous HF in vacuo. The resulting suspension was stirred briefly, and the solid was allowed to settle. The supernatant solution was decanted into the sidearm. HF was recondensed into the main arm, and the washing process was repeated four times. After washing, 0.610 g of [Fe(CO)$_6$][SbF$_6$]$_2$ was obtained in crystalline form, which implied a yield of 98%. The isotopomer [Fe(^{13}CO)$_6$][SbF$_6$] was obtained in an identical manner from [Fe(^{13}CO)$_6$][Sb$_2$F$_{11}$]$_2$. [Fe(CO)$_6$][SbF$_6$]$_2$ is a colorless moisture-sensitive crystalline solid which decomposed with evolution of CO when heated beyond 150 °C. The residue was identified as Fe[SbF$_6$]$_2$ by its vibrational spectrum.[28] Band positions, intensities, and assignments of the [SbF$_6$]$^-$ anion are the following: IR, ($\nu_1 + \nu_3$) 1331(vw), 1310(vw); ($\nu_2 + \nu_3$), 1248(w), 1227(vw,sh); ($\nu_4 + 2\nu_6$), 683-(w,sh); νSbF(ν_3,T$_{1u}$), 665(vs); δSbF(ν_4, T$_{1u}$), 292(vs); (ν_5, T$_{2g}$), 282-(w,sh); (ν_6, T$_{2u}$), 196(vw,sh); Raman, νSbF(ν_1,A$_{1g}$) 652.6(vs), (ν_2, E$_g$) 570.7(m), δSbF(ν_5, T$_{2g}$) 281.4(s).

Results and Discussion

(a) Synthesis. As previously reported by us,[29] [Fe(CO)$_6$]-[Sb$_2$F$_{11}$]$_2$ may be obtained by the oxidative carbonylation of Fe(CO)$_5$ in liquid antimony(V) fluoride as reaction medium with either Cl$_2$ or AsF$_5$ as external oxidizing agents according to the following:
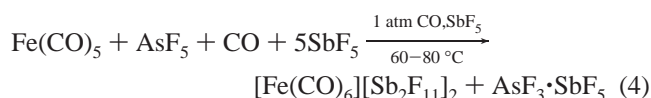
$$\text{Fe(CO)}_5 + \text{Cl}_2 + \text{CO} + 6\text{SbF}_5 \xrightarrow[40-80\,°C]{1\ \text{atm CO,SbF}_5} [\text{Fe(CO)}_6][\text{Sb}_2\text{F}_{11}]_2 + 2\text{SbF}_4\text{Cl} \quad (3)$$

or

$$\text{Fe(CO)}_5 + \text{AsF}_5 + \text{CO} + 5\text{SbF}_5 \xrightarrow[60-80\,°C]{1\ \text{atm CO,SbF}_5} [\text{Fe(CO)}_6][\text{Sb}_2\text{F}_{11}]_2 + \text{AsF}_3\cdot\text{SbF}_5 \quad (4)$$

As the vibrational spectra in the CO-stretching region indicate, [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ is produced by these routes; however, there are three serious problems affecting both synthetic approaches:

(i) Bulk magnetic susceptibility measurements on [Fe(CO)$_6$]-[Sb$_2$F$_{11}$]$_2$ obtained by either route reveal the presence of substantial amounts of paramagnetic material. While pure [Fe-(CO)$_6$][Sb$_2$F$_{11}$]$_2$ is found in the course of this study to be essentially diamagnetic, commensurate with an Fe^{II} low spin d^6 configuration and a ^{1}A$_{1g}$ octahedral ground state, the observed paramagnetism is attributed to Fe[SbF$_6$]$_2$,[28] whose magnetic behavior will be discussed below.

(ii) The solid byproducts formulated as SbF$_4$Cl[53] and AsF$_3$·SbF$_5$[54] are difficult to remove from the reaction mixture. Heating of the sample to remove SbF$_4$Cl by sublimation results in further irreversible decomposition to Fe[SbF$_6$]$_2$.[28] The attempted elution of AsF$_3$ from the adduct AsF$_3$·SbF$_5$[54] by repeated washing with SO$_2$, to produce thermally less stable SO$_2$·SbF$_5$,[55] results in partial removal of SbF$_5$ from the anion [Sb$_2$F$_{11}$]$^-$ to give [SbF$_6$]$^-$.

(iii) In samples of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ obtained by oxidation of Fe(CO)$_5$ with an excess of Cl$_2$,[29] an additional complication is encountered. An IR band at 2256 cm^{-1} is observed, which has been erroneously attributed to [Fe(CO)$_6$]$^{3+}$,[29] because [Ir-(CO)$_6$]$^{3+}$ has the IR active fundamental ν_6 (T$_{1u}$) at 2254 cm^{-1}.[56] This band is now unambiguously identified as the CO-stretching vibration of [ClCO]$^+$,[57−59] by a complete vibrational analysis of this novel cation.[57]

In summary, previously reported synthetic routes to [Fe(CO)$_6$]-[Sb$_2$F$_{11}$]$_2$[29] lead to complex product mixtures and the reported separation and purification procedures[25b,29] are inadequate. Hence a substantially new synthetic method is developed here. The failure to produce any evidence for [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$ by reductive carbonylation of either Fe(SO$_3$F)$_3$[60] or FeCl$_3$[61] in liquid SbF$_5$, while Ru(SO$_3$F)$_3$[62] and Os(SO$_3$F)$_3$[63] are cleanly converted to [M(CO)$_6$][Sb$_2$F$_{11}$]$_2$, M = Ru, Os[27] provides an important clue. Both M(SO$_3$F)$_3$, M = Ru,[62] or Os,[63] are low spin complexes and have between 300 and 80 K magnetic properties consistent with a ^{2}T$_{2g}$ octahedral ground state.[62,63] On the other hand, both Fe(SO$_3$F)$_3$[60] and FeCl$_3$[61] are high spin complexes with magnetic properties suggestive of a ^{6}A$_{1g}$ ground state. With both metal σ-symmetry d-orbitals (dz^2 and dx^2-y^2) singly occupied, reduction to Fe$^{(II)}$ must bring about a change in spin state before carbonylation can occur to give octahedral [Fe(CO)$_6$]$^{2+}$ with a ^{1}A$_{1g}$ ground state. This is clearly not the case, because high spin Fe[SbF$_6$]$_2$[28] forms quantitatively. Since other potential Fe-(II) or Fe(III) precursors such as FeCl$_2$, FeF$_2$, or FeF$_3$ also have the metal in a high spin configuration,[64] it appears that neither

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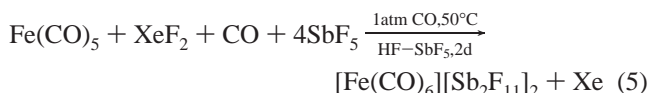(61) Starr, C.; Bitter, F.; Kaufmann, A. R. *Phys. Rev.* **1940**, *58*, 977.

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solvolytic nor reductive carbonylation in liquid SbF_5, the two most effective synthetic methods,[25b] will be successful here.

On the other hand, in the reductive carbonylation of $M(SO_3F)_3$, M = Ru, Os, to $[M(CO)_6]^{2+}$ [27] no change in spin state is necessary. In addition, compounds of the type $M[SbF_6]_2$, M = Ru, Os, analogous to $Fe[SbF_6]_2$ appear to be unknown.[65] This leaves the oxidative carbonylation of diamagnetic $Fe(CO)_5$[66] as the only promising alternative. To overcome the above-mentioned difficulties when AsF_5 or Cl_2 are used as external oxidizing agents,[29] two drastic departures of previous practices are implemented; xenon(II) fluoride, XeF_2, is used as oxidizing agent and SbF_5 is replaced by the conjugate superacid HF$-$SbF$_5$[23,24] as strongly ionizing reaction medium. The overall reaction proceeds according to the following:

$$Fe(CO)_5 + XeF_2 + CO + 4SbF_5 \xrightarrow[\text{HF}-\text{SbF}_5, 2d]{\text{1atm CO,50°C}}$$
$$[Fe(CO)_6][Sb_2F_{11}]_2 + Xe \quad (5)$$

The removal of the volatile byproduct Xe presents no problem, and $[Fe(CO)_6][Sb_2F_{11}]_2$ is obtained in the form of sizable colorless crystals, suitable for spectroscopic studies and single-crystal X-ray diffraction.

The exact course of the formation reaction of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$ is unclear. Initial formation of $Fe(CO)_4F_2$ or the ionized species $[Fe(CO)_5F]^+$ and $[Fe(CO)_4F]^+$ may be postulated, even though neither species is isolable.[67] Related compounds such as $Fe(CO)_4X_2$, X = Cl, Br, or I,[68−70] or ions such as $[Fe(CO)_5X]^+$, X = Cl, Br, NO,[21] are known. Attempts to obtain information on the intermediates in HF$-$SbF$_5$ solution by ^{13}C or ^{19}F NMR are hindered by line broadening on account of the presence of paramagnetic Fe^{2+} species. It appears that, even with improved synthetic conditions, the formation reaction of $Fe[SbF_6]_2$[28] remains in competition with that of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$. However, with the use of HF$-$SbF$_5$ the latter is now formed in a much higher yield than before,[29] judging by the relative intensities of the bands due to CO-stretching vibrations. $[Fe(CO)_6][Sb_2F_{11}]_2$ is isolated in form of single crystals and is cleanly separated from the byproduct $Fe[SbF_6]_2$. The isolation of single crystals of $[Sb_2F_{11}]^-$ salts of homoleptic superelectrophilic metal carbonyl cations from HF$-$SbF$_5$, reported here for the first time, is not restricted to $[Fe(CO)_6][Sb_2F_{11}]_2$. Two recent, so far unpublished examples involve the isostructural pairs $[M(CO)_4]^{2+}$, M = Pd, Pt,[71] and $[M(CO)_6]^{2+}$, M = Ru, Os,[72] all with $[Sb_2F_{11}]^-$ as anion. The latter study completes the structural characterization of the triad $[M(CO)_6][Sb_2F_{11}]_2$, M = Fe, Ru, Os. All three salts are found to be isostructural.[72]

The use of anhydrous hydrogen fluoride as a protonic solvent has an additional unexpected advantage: repeated washing of crystalline $[Fe(CO)_6][Sb_2F_{11}]_2$ allows its transformation into the $[SbF_6]^-$ salt, which is again obtained in the form of single crystals, suitable for a molecular structure determination (see eq 2). The salt $[Fe(CO)_6][SbF_6]_2$ becomes the first fully

characterized example, where a homoleptic superelectrophilic metal carbonyl cation is stabilized by $[SbF_6]^-$ as counterion rather than by the ubiquitous $[Sb_2F_{11}]^-$.[25b] The conversion of $[Fe(CO)_6][Sb_2F_{11}]_2$ into the corresponding $[SbF_6]^-$ salt may also be affected by washing with SO_2 or HSO_3F and even by controlled thermal degradation. However, none of these alternative routes is clean and produces a crystalline material. How far the novel conversion of $[Sb_2F_{11}]^-$ into $[SbF_6]^-$ salts described here may be applied to other $[M(CO)_n][Sb_2F_{11}]_m$[25b] salts remains to be seen. As far as the substitution of liquid SbF_5 by the conjugate superacid HF$-$SbF$_5$[23,24] is concerned, preliminary indications are that most carbonylation reactions reviewed by us recently[25b] are more easily performed in HF$-$SbF$_5$. While lower reaction temperatures, shorter reaction times, reduced separation problems, and the formation of crystalline reaction products are clear advantages, there is an important disadvantage: glass is no longer tolerable as construction material for reactors and vacuum lines and its replacement by metal or better by fluorocarbon polymers is necessary. The improved synthesis of $[Fe(CO)_6][Sb_2F_{11}]_2$ reported here is experimentally far more demanding than the previously described approach.[29] It requires rather specialized and more expensive equipment, as discussed in the Experimental Section. The technical and experimental difficulties encountered are similar to those described previously when using superacids and in particular anhydrous HF[73] or HF$-$SbF$_5$ in synthetic applications.[23,24]

Both $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$ have comparable thermal stabilities to approximately 150 °C. Their modes of decomposition differ. When $[Fe(CO)_6][Sb_2F_{11}]_2$ is heated to 150 °C, a clear colorless liquid, identified as SbF_5 by its spectroscopic and physical properties,[73] is formed initially. On further heating, the evolution of CO is noted. The initial decomposition may be formulated as the following:

$$[Fe(CO)_6][Sb_2F_{11}]_2 \underset{25\,°C}{\overset{>140\,°C}{\rightleftharpoons}} [Fe(CO)_6][SbF_6]_2 + 2SbF_5 \quad (6)$$
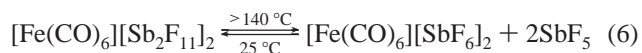
The subsequent step is irreversible and proceeds according to the following:

$$[Fe(CO)_6][SbF_6]_2 \xrightarrow{>140-150\,°C} Fe[SbF_6]_2 + 6CO \quad (7)$$
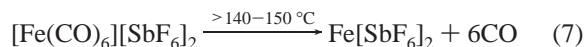
The second decomposition step is more easily studied when starting from $[Fe(CO)_6][SbF_6]_2$, where formation of SbF_5 is not observed. The approximate decomposition rates in mole % per minute increase from 0.01 at 140−150 °C to 0.06 at 160−170 °C, to 0.2 at 170−180 °C, to 1 at 190−200 °C, and to ∼5 at 200−205 °C. From these data a rough estimate of the Arrhenius activation energy E_a of 180−210 kJ mol^{-1} and of the pre-exponential Arrhenius factor of 10^{18} s^{-1} is obtained with $\Delta S^‡$ approximately 100 J mol^{-1} K^{-1}. The solid residue is identified as $Fe[SbF_6]_2$ by its vibrational spectrum.[28] No intermediates of the type $[Fe(CO)_n][SbF_6]_2$ with n between 1 and 5 are detectable. Hence, the oxidative carbonylation of $Fe(CO)_5$ in either SbF_5 or HF$-$SbF$_5$ and subsequent thermal decomposition of the intermediates provide an alternative route to $Fe[SbF_6]_2$. However, this rather involved procedure offers no advantage over other previously reported methods.[28,48,65]

A brief comment concerns the possible existence of $[Fe(CO)_6]^{3+}$. As discussed already, its suggested formation during the oxidation of $Fe(CO)_5$ with Cl_2[29] is clearly in error. All

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[Fe(CO)₆][Sb₂F₁₁]₂ and [Fe(CO)₆][SbF₆]₂

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Table 1. Crystallographic Data for the Structure Determination of $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$ at 300 K

	$[Fe(CO)_6][Sb_2F_{11}]_2$	$[Fe(CO)_6][SbF_6]_2$
empirical formula	$C_6F_{22}FeO_6Sb_4$	$C_6F_{12}FeO_6Sb_2$
formula weight	1128.9	695.4
crystal system	monoclinic	tetragonal
space group	Nr.14, $P\,2_1/n$	Nr.128, $P\,4/mnc$
color of crystal	colorless	colorless
a [Å]	9.751(1)	8.258(1)
b [Å]	12.457(1)	8.258
c [Å]	10.542(1)	12.471(2)
β [deg]	110.63(1)	90
V [Å³]	1198.4(2)	850.5(2)
Z	2	2
goodness-of-fit on F^2	0.843	1.03
R_1 [$I > 2\sigma(I)$]	0.0282	0.0259
wR_2	0.0532	0.0668

subsequent attempts to oxidize $[Fe(CO)_6]^{2+}$ in HF solution with XeF_2, F_2, or NiF_4[74] have failed. As discussed below, magnetic measurements between 4 and 300 K on impure samples of [Fe-$(CO)_6][Sb_2F_{11}]_2$ are consistent with the presence of $Fe[SbF_6]_2$ as the only paramagnetic species in the reaction mixture. Hence $[Ir(CO)_6]^{3+}$[56] remains as the sole homoleptic carbonyl cation with the metal in a 3+ oxidation state.

The enormous advantage the new synthetic methodology holds over the previously reported methods (reactions 3 and 4),[29] in particular the use of HF–SbF_5, is most convincingly demonstrated by the determination of the molecular structures of both $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$ to be discussed next. In summary, the $[Fe(CO)_6]^{2+}$ cation occupies a unique position among the homoleptic metal carbonyl cations for three reasons:

(i) It is the first isolated superelectrophilic carbonyl cation formed by a 3d-metal.

(ii) It is so far the only superelectrophilic carbonyl cation[25b] with $[SbF_6]^-$ as well as $[Sb_2F_{11}]^-$ as counterions.

(iii) It is, as the next sections will show, the most extensively characterized homoleptic carbonyl cation to date.

The ability of both $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ to function as counterions for $[Fe(CO)_6]^{2+}$ suggests that both anions are comparably weak nucleophiles. This conclusion has been reached by us some time ago,[75] based on ^{119}Sn Mössbauer data for dimethyltin(IV) salts of strong protonic acids and superacids. In addition, the lattice energy should be larger for $[Fe(CO)_6]$-$[SbF_6]_2$ than for the $[Sb_2F_{11}]^-$ salt, considering anion sizes only. Hopefully more $[M(CO)_n][SbF_6]_m$ salts can be obtained by the novel conversion reaction described here. This will certainly simplify the vibrational analysis of the salts.

(b) The Crystal and Molecular Structure of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$. Crystallographic data and details on the structure determinations are collected in Table 1. Selected bond distances for both salts are listed in Table 2. The molecular structures of $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6]$-$[SbF_6]_2$, showing a formula unit and the numbering system used, are found in Figures 1 and 2.

$[Fe(CO)_6][SbF_6]_2$ crystallizes in a tetragonal space group $P4/mnc$ (no. 128). Not surprisingly both the $[SbF_6]^-$ anion and the $[Fe(CO)_6]^{2+}$ cation show very slight distortion from regular octahedral geometry. The anion (site symmetry 222) is compressed, while the cation, judging by the Fe–C bond distances,

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Table 2. Selected Bond Distances [Å] and Angles [deg] for $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$

	$[Fe(CO)_6][Sb_2F_{11}]_2$		
Fe–C1 (2×)	1.911(5)	C1–O1 (2×)	1.103(5)
Fe–C2 (2×)	1.912(5)	C2–O2 (2×)	1.102(5)
Fe–C3 (2×)	1.910(5)	C3–O3 (2×)	1.107(5)
Sb1–F1	2.053(3)	Sb2–F1	1.998(3)
Sb1–F2	1.850(3)	Sb2–F7	1.836(4)
Sb1–F3	1.835(3)	Sb2–F8	1.864(3)
Sb1–F4	1.842(3)	Sb2–F9	1.847(3)
Sb1–F5	1.824(3)	Sb2–F10	1.843(3)
Sb1–F6	1.869(3)	Sb2–F11	1.810(3)
C1–Fe–C2 (2×)	89.2(2)	C1–Fe–C2 (2×)	90.8(2)
C2–Fe–C3 (2×)	88.9(2)	C2–Fe–C3 (2×)	91.1(2)
C3–Fe–C1 (2×)	89.8(2)	C3–Fe–C1 (2×)	90.2(2)
C1–Fe–C1	180	C2–Fe–C2	180
C3–Fe–C3	180	Fe–C1–O1 (2×)	178.1(4)
Fe–C2–O2 (2×)	177.5(4)	Fe–C3–O3 (2×)	179.4(4)
F1–Sb1–F3	86.2(2)	F1–Sb2–F8	84.8(1)
F1–Sb1–F4	86.2(1)	F1–Sb2–F9	87.2(1)
F1–Sb1–F5	84.3(2)	F1–Sb2–F10	87.3(2)
F1–Sb1–F6	83.3(1)	F1–Sb2–F11	85.7(2)
F2–Sb1–F3	96.4(2)	F7–Sb2–F8	92.0(2)
F2–Sb1–F4	96.6(2)	F7–Sb2–F9	91.4(2)
F2–Sb1–F5	93.1(2)	F7–Sb2–F10	95.7(2)
F2–Sb1–F6	94.0(2)	F7–Sb2–F11	95.8(2)
F3–Sb1–F4	89.7(2)	F8–Sb2–F9	88.4(2)
F4–Sb1–F5	92.3(2)	F9–Sb2–F10	86.8(2)
F5–Sb1–F6	89.4(2)	F10–Sb2–F11	92.4(2)
F6–Sb1–F3	87.0(2)	F11–Sb2–F8	91.4(2)
F1–Sb1–F2	176.2(1)	F1–Sb2–F7	176.6(2)
F3–Sb1–F5	170.1(2)	F8–Sb2–F10	171.0(2)
F4–Sb1–F6	169.2(1)	F9–Sb2–F11	172.9(2)
Sb1–F1–Sb2	148.5(2)		

	$[Fe(CO)_6][SbF_6]_2$		
Fe–C1 (2×)	1.917(7)	C1–O1 (2×)	1.096(9)
Fe–C2 (4×)	1.903(6)	C2–O2 (4×)	1.114(8)
Sb–F1 (4×)	1.852(3)	Sb–F2 (2×)	1.832(3)
C1–Fe–C2 (8×)	90	C2–Fe–C2 (4×)	90
C1–Fe–C1	180	C2–Fe–C2 (2×)	180
Fe–C1–O1 (2×)	180	Fe–C2–O2 (4×)	178.9(5)
F1–Sb–F1 (2×)	88.3(1)	F1–Sb–F1 (2×)	91.9(1)
F1–Sb–F2 (4×)	87.2(1)	F1–Sb–F2 (4×)	92.8(1)
F1–Sb–F1 (2×)	174.4(2)	F2–Sb–F2	180
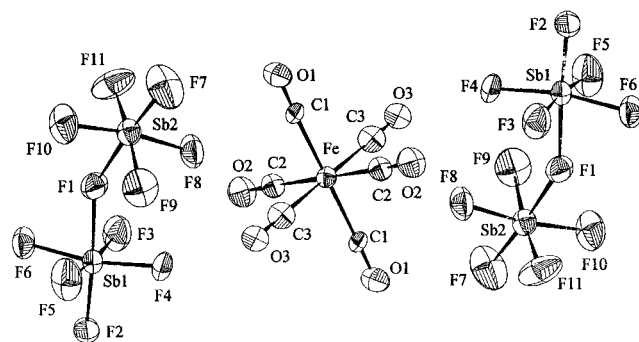
Figure 1. The molecular structure of $[Fe(CO)_6][Sb_2F_{11}]_2$: formula unit, 50% probability ellipsoids.

is elongated along the c-axis (site symmetry $4/m$). The structure type is related to the CaF_2 prototype, with the $[SbF_6]^-$ occupying all available tetrahedral holes.

$[Fe(CO)_6][Sb_2F_{11}]_2$ crystallizes in the monoclinic spacegroup $P2_1/n$ (no. 14). All other so far structurally characterized $[Sb_2F_{11}]^-$ salts with dipositive homoleptic metal carbonyl cations belong to this space group as well. The list includes in addition to $[Fe(CO)_6][Sb_2F_{11}]_2$ the isostructural pair $[M(CO)_6][Sb_2F_{11}]_2$, M = Ru, Os,[72] the group 10 salts $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt[71] and in group 12 $[Hg(CO)_2][Sb_2F_{11}]_2$.[76] In the group 8 compounds $[M(CO)_6][Sb_2F_{11}]_2$, M = Fe, Ru, Os, as well as in
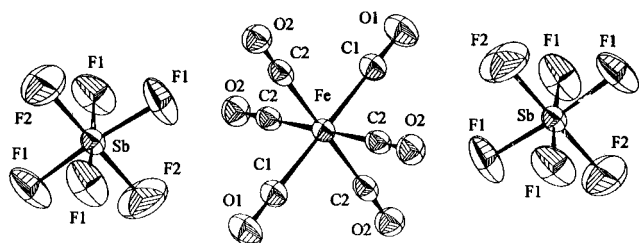
Figure 2. The molecular structure of $[Fe(CO)_6][SbF_6]_2$: formula unit, 50% probability.

Figure 3. Selected significant interionic contacts in $[Fe(CO)_6][Sb_2F_{11}]_2$.

$[Hg(CO)_2][Sb_2F_{11}]_2$,[76] the cations have crystallographic inversion symmetry. Hence, both $[Sb_2F_{11}]^-$ anions are symmetry related and have identical bond parameters. This is not the case for the anion pairs in $[M(CO)_4][Sb_2F_{11}]_2$,[71] M = Pd, Pt, and for $[Ir(CO)_5Cl][Sb_2F_{11}]_2$[56] where two structurally different $[Sb_2F_{11}]^-$ anions are encountered in all three compounds.

In all cases discussed here, the $[Sb_2F_{11}]^-$ ions are distorted from ideal D_{4h} symmetry, as, for example, found in $[H_3F_2]$-$[Sb_2F_{11}]$.[77] There are primarily two distortional processes involved:

(i) bending of the two SbF_5 moieties about the bridging F atom, expressed in terms of a Sb–F–Sb bridge angle, and

(ii) rotation of the two SbF_4 planar groups relative to each other, expressed in terms of a dihedral angle.

For $[Fe(CO)_6][Sb_2F_{11}]_2$, bridge and dihedral angles of 148.5° and 36.8° are found, respectively. Identical bridge- and dihedral angles are found for the isostructural salts $[M(CO)_6][Sb_2F_{11}]$, M = Ru, Os. Very similar distortions are found for $[H_3O]$-$[Sb_2F_{11}]$,[26] which has three crystallographically different $[Sb_2F_{11}]^-$ anions in the unit cell of a rather complex polymeric structure. Here the cause for the distortions of the $[Sb_2F_{11}]^-$ anions and their dissimilarity is seen in various types of interionic asymmetric O–H⋯F hydrogen bonds.[26] There is an interesting parallel between the cations $[H_3O]^+$ and $[Fe(CO)_6]^{2+}$: Both form thermodynamically stable, structurally characterized salts with $[Sb_2F_{11}]^-$ [26] as well as with $[SbF_6]^-$ [78,79] as counteranions. In both types of salts the $[Sb_2F_{11}]^-$ anions are distorted in a similar manner, while the crystal structures of $[Fe(CO)_6][SbF_6]_2$ and $[H_3O][SbF_6]$[79] indicate tetragonal and cubic symmetry, respectively, and the $[SbF_6]^-$ anions depart only slightly from O_h symmetry.[79]

The octahedral cations in $[Fe(CO)_6][Sb_2F_{11}]_2$ and in $[Fe(CO)_6]$-$[SbF_6]_2$ are virtually identical. The average bond distances for the $[Sb_2F_{11}]^-$ salt, Fe–C_{avg} of 1.911(5) Å and C–O_{avg} of 1.104-(5) Å, compare very closely to and within the esd values of 1.908(6) and 1.108(6) Å, respectively, found for $[Fe(CO)_6]$-$[SbF_6]_2$. The observed C–O bond distances merit little discussion beyond the statement that they appear to be shorter than that in free CO (1.1281 Å)[80] and that they rank at the lower end of 10 022 data collected in the Cambridge compilation[81] where the lower quartile value q_l is 1.132 Å. In metal carbonyl cations[25b] the strength of the CO bond is better probed by vibrational spectroscopy as will be discussed subsequently.

The Fe–C_{avg} bond distances of 1.908(6) and 1.911(5) Å are unusually long compared to the q_u value of 1.801 Å based on 2572 data contained in the Cambridge index.[81] Agreement with bond distances from ab initio calculations is excellent to fair. In the study by Jonas and Thiel[31] Fe–C values of 1.903 and 1.905 Å are obtained for $[Fe(CO)_6]_g^{2+}$, depending on the computational method employed. A DFT study by Ziegler et al.[38] reports an Fe–C bond length of 1.895 Å. Calculated C–O bond distances fall in both studies between 1.129[38] and 1.140[31] Å and are in fact longer than in free CO.[80] This underscores the point that, in compounds of this type with very strong C–O bonds, accurate bond distances are equally difficult to determine and to calculate.

There are, for the $[Fe(CO)_6]^{2+}$ cation in both salts, very slight angular distortions from regular octahedral symmetry. In $[Fe(CO)_6][Sb_2F_{11}]_2$ the C–Fe–C angles depart from 90° by 0.2° to 1.1° while the Fe–C–O angles range from 179.4(4)° to 177.5(4)°. In $[Fe(CO)_6][SbF_6]_2$ only four of the six Fe–C–O angles depart with 178.9(5)° very slightly from linearity. Similar departures from linearity are found for $[Hg(CO)_2][Sb_2F_{11}]_2$[76] and $[M(CO)_4][Sb_2F_{11}]_2$,[71] M = Pd, Pt, where linear[76] and square planar[71] cations are present. As the detailed vibrational analyses[71,76] show, the angular distortions and the tetragonal distortion of the $[Fe(CO)_6]^{2+}$ cation in the $[SbF_6]^-$ salt are insufficient to destroy the inversion symmetry and affect the mutual exclusion rule for IR and Raman active vibrations in all instances.[71,72,76]

In summary, the $[Fe(CO)_6]^{2+}$ cation is essentially octahedral. Its relevant bond parameters (bond length and angles) are virtually identical in both $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6]$-$[SbF_6]_2$. The observed long Fe–C and short C–O bonds suggest that CO is primarily σ-bonded to Fe^{2+}, with π-back-bonding minimal. In agreement with a recent theoretical analysis[82] and our findings for other homoleptic metal carbonyl cations,[25b] the C–O bond in $[Fe(CO)_6]^{2+}$ is strongly polarized with a positive partial charge on the carbon atom.

As in other salts of homoleptic metal carbonyl cations with $[Sb_2F_{11}]^-$ as counteranion, there are in $[Fe(CO)_6][Sb_2F_{11}]_2$, but also to a lesser extent in $[Fe(CO)_6][SbF_6]_2$ a number of secondary[83] interionic contacts. These contacts are shown for the respective formula units of both salts in Figures 3 and 4. They differ from other such contacts observed previously between $[Sb_2F_{11}]^-$ and various homoleptic metal carbonyl cations[25] like linear $[Hg(CO)_2]^{2+}$ [76] and square planar $[M(CO)_4]^{2+}$,[71] M = Pd, Pt, in four significant ways:

(i) The contacts are now due mainly to C⋯F and to a lesser extent to O⋯F interactions.

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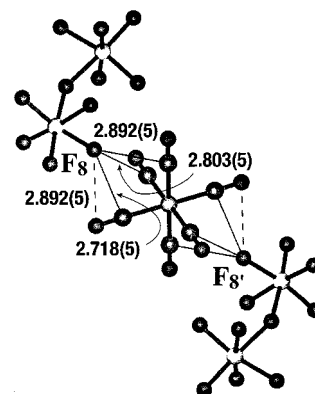
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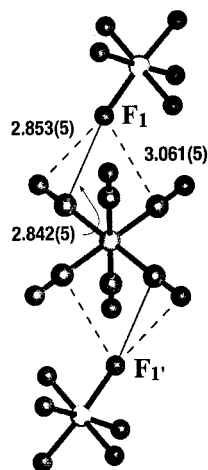
[Fe(CO)₆][Sb₂F11]₂ and [Fe(CO)₆][SbF₆]₂

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Figure 4. Selected significant interionic contacts in $[Fe(CO)_6][SbF_6]_2$.

Figure 5. Vibrational spectra of $[Fe(CO)_6][Sb_2F_{11}]_2$.

Figure 6. Vibrational spectra of $[Fe(CO)_6][SbF_6]_2$.

(ii) The contact distances are longer and the interactions presumably weaker.

(iii) There are within the formula unit fewer C···F contacts per CO group (about 1) compared to 5 such contacts for [Hg-(CO)₂][Sb₂F₁₁]₂[76] and approximately 3 in [M(CO)₄][Sb₂F₁₁]₂-71, M = Pd, Pt.

(iv) Multiple F···CO contacts involving up to four per F atom in the [Sb₂F₁₁]⁻ salt are observed. Previously only single or double (bifurcated) contacts have been observed.[71,76]

The strength of secondary interactions is customarily[83] judged by comparison to the sum of the van der Waals radii[84] Σr_{vdw} of the atoms involved which have values of 3.17 and 2.99 Å for C···F and O···F interactions, respectively. In case of [Fe(CO)₆]-[Sb₂F₁₁]₂, there are two pairs of significant C···F contacts at 2.718 and 2.803 Å, respectively, and a third set of marginal interactions at 2.870 Å. The interactions involve all six C atoms of the $[Fe(CO)_6]^{2+}$ cation and both symmetry-related F₈ atoms of the anions (see Figure 3).

In $[Fe(CO)_6][SbF_6]_2$ weaker and fewer interionic C···F contacts of 2.842 and 3.061 Å are observed together with a pair of O···F contacts at 2.853. The contacts involve only four of the six CO groups. The remaining two CO groups are trans to each other and have slightly longer Fe—C (1.917(7) Å) and shorter C—O (1.096(9) Å) bonds. The determined crystallographic site symmetry of 4/m (C_{4h}) for the $[Fe(CO)_6]^{2+}$ cation in the [SbF₆]⁻ salt necessitates that two symmetry-related axial Fe—C—O fragments be linear. The four symmetry equivalent Fe—C—O fragments with bond angles of 178.9(5)° deviate only very slightly from linearity. It hence seems that slight departures from linearity observed for this M—C—O group both in [Fe-(CO)₆]²⁺ cations as well as in [Hg(CO)₂]²⁺[76] and in [M-(CO)₄]²⁺,[71] M = Pd, Pt, are caused by significant interionic F···C contacts.

It can be concluded that, for the octahedral $[Fe(CO)_6]^{2+}$ cation, stabilization by secondary contacts to the anion is less important than in case of linear [Hg(CO)₂][Sb₂F₁₁]₂[76] or square planar [M(CO)₄][Sb₂F₁₁]₂[71],M = Pd, Pt, compounds on account of a greater intrinsic stability of $[Fe(CO)_6]^{2+}$, which is in agreement with theoretical predictions for gaseous [Fe-(CO)₆]g²⁺.[38]

(c) Vibrational Spectra of [Fe(CO)₆][Sb₂F₁₁]₂ and [Fe-(CO)₆][SbF₆]₂. The IR and Raman spectra of [Fe(CO)₆][Sb₂F₁₁]₂ and [Fe(CO)₆][SbF₆]₂ are depicted in Figures 5 and 6, respectively. The vibrational wavenumbers of the $[Fe(CO)_6]^{2+}$ cation and its ¹³C isotopomer are listed in Table 3. The numbering
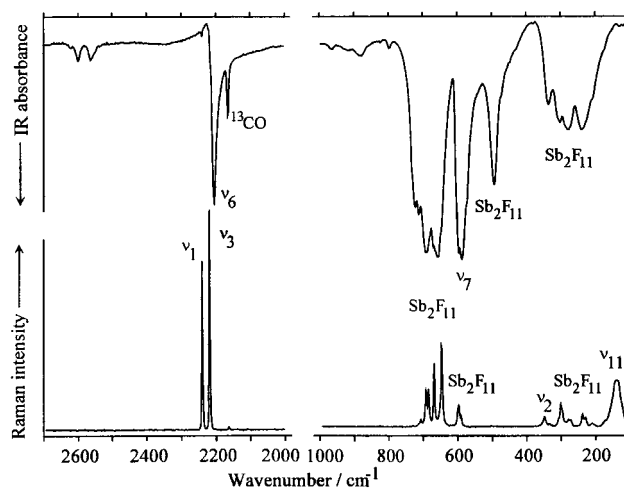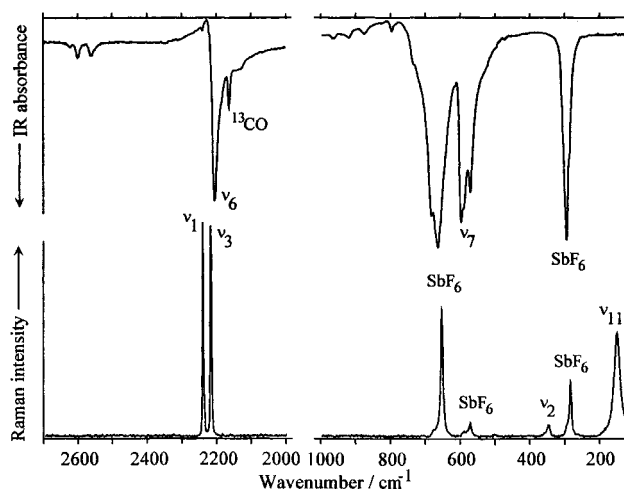
used for the fundamentals of $[Fe(CO)_6]^{2+}$ is adopted from a vibrational study of the neutral metal hexacarbonyls M(CO)₆, M = Cr, Mo, W.[32,33] Of these, Cr(CO)₆ is isoelectronic and isosteric with $[Fe(CO)_6]^{2+}$, which provides help in the subsequent band assignment. Comparison to the early study[32,33] is particularly useful because vibrational data are obtained on gaseous, solid, and dissolved (in CCl₄) samples,[32] while our study is restricted to solid-state compounds.

There are four noteworthy features in the vibrational spectra of the $[Fe(CO)_6]^{2+}$ salts:

(i) The relative intensities of bands in the CO-stretching region have increased relative to bands in the 700—550 cm⁻¹ region. There is a marked difference between the spectrum of [Fe(CO)₆]-[Sb₂F₁₁]₂ published previously[29] and the one shown in Figure 5 with respect to band intensities.

(ii) Band positions and intensities of bands due to $[Fe(CO)_6]^{2+}$ in both salts are nearly identical. Cation bands are easily identified with the help of ¹³C substitution.

(iii) Vibrational bands of the [SbF₆]⁻ anion are much simpler and more intense than those of [Sb₂F₁₁]⁻.

(iv) The IR spectra of both salts show a fair number of overtones, which are similar in band positions and intensities to combination bands found and assigned for Cr(CO)₆.[32,33] These combination bands are useful in locating inactive fundamentals (T₁g, T₂u) and in assigning low-intensity bands of the [Fe-(CO)₆]²⁺ cation.

The assignment of the fundamental vibrations of the [Fe-(CO)₆]²⁺ cation is for the most part straightforward. Of the four

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Table 3. Vibrational Data for $[Fe(CO)_6]^{2+}$ in $[Fe(CO)_6][Sb_2F_{11}]_2$, $[Fe(^{13}CO)_6][Sb_2F_{11}]_2$, $[Fe(CO)_6][SbF_6]_2$, and $[Fe(^{13}CO)_6][SbF_6]_2$

assignment ν^a	symm. species	$[Fe(CO)_6][Sb_2F_{11}]_2$ IR	Ra	$[Fe(CO)_6][SbF_6]_2$ IR	Ra	$[Fe(^{13}CO)_6][Sb_2F_{11}]_2$ IR	Ra	$[Fe(^{13}CO)_6][SbF_6]_2$ IR	Ra
$\nu_1 + \nu_6$		4441(vw)						4341(vw)	
$\nu_3 + \nu_6$		4402(vw)						4303(vw)	
$\nu_1 + \nu_7$		2828(vw)		2835(vw)		2766(vw)			
$\nu_3 + \nu_7$				2812(vvw)		2745(vvw)			
$\nu_1 + \nu_{12}, \nu_6 + \nu_{10}$		2707(vvw)		2703(vvw)		2635(vvw)			
$\nu_3 + \nu_{12}$		2688(vvw)		2688(vvw)		2621(vvw)			
$\nu_1 + \nu_8$		2623(vw)		2623(vw)		2564(vw)		2563(vw)	
$\nu_3 + \nu_8$		2600(w)		2600(w)		2542(w)		2543(w)	
$\nu_6 + \nu_4$		2564(w)		2562(w)		2509(w)		2509(w)	
$\nu_6 + \nu_2$		2551(w,sh)		2551(w,sh)		2499(w,sh)		2500(w,sh)	
$\nu_6 + \nu_5$				2535(vvw)		2476(vvw)			
$\nu_3 + \nu_9$		2386(vvw)		2390(vvw)					
$\nu_6 + \nu_{11}$		2335(vvw)		2348(vvw)					
$\nu_3 + \nu_{13}$				2336(vvw,sh)					
$\nu_1, \nu CO$	A_{1g}		2241.2(vs)		2241.9(vs)		2189.7(vs)		2190.5(vs)
$\nu_3, \nu CO$	E_g		2219.5(vs)		2219.0(vs)		2169.0(vs)		2168.4(vs)
$\nu_6, \nu CO$	T_{1u}	2204(vs)		2205(vs)		2154(vs)		2155(vs)	
$\nu_7 + \nu_{10}$				1088(vvw)					
$\nu_{10} + \nu_{12}$		968(w)		967(w)		935(w)		933(w)	
$\nu_7 + \nu_5$		922(w)		923(w)		897(w)		899(w)	
$\nu_8 + \nu_{10}$		881(w)		878(w)		856(w)		855(w)	
$\nu_5 + \nu_{12}$		799(w)		799(w)		775(w)		774(w)	
$\nu_4 + \nu_8$				738(vw)					
$\nu_{11} + \nu_{12}$				615(vw)					
				(598(mw,sh)				(589(w,sh)	
$\nu_7, \delta FeCO$	T_{1u}	586(vs)		{590(vs)		571(vs)		{576(vs)	
				(570(mw,sh)				{566(w,sh)	
$\nu_{10}, \delta FeCO$	T_{2g}		500.9(vvw)		499.8(vvw)					
$\nu_{12}, \delta FeCO$	T_{2u}	468(vw)		470(vw)		454(vw)			
$\nu_8, \nu FeC$	T_{1u}	380(w)		382(w)		374(w)		375(w)	
$\nu_4, \nu FeC$	E_g		361(w,sh)		357(vw,sh)		356(vw,sh)		353(vw,sh)
$\nu_2, \nu FeC$	A_{1g}		347.1(m)		345.3(m)		342.7(m)		341.6(m)
$\nu_9, \delta CFeC$	T_{1u}	170(vw)		171(vw)		170(vw)		171(vw)	
$\nu_{11}, \delta CFeC$	T_{2g}		138(s,br)		148(s,br)		138(s,br)		148(s,br)
$\nu_{13}, \delta CFeC$	T_{2u}	114(vw)				114(vw)			

^{a} Numbering of fundamentals from ref 32.

IR active fundamentals of octahedral $[Fe(CO)_6]^{2+}$, both ν_6 (ν C−O) and ν_7 (δ Fe−CO) are very intense. For ν_7, pronounced fine structure is observed in the spectrum of $[Fe(CO)_6][SbF_6]_2$, which is less noticeable for $[Fe(CO)_6][Sb_2F_{11}]_2$, where a shoulder at 599 cm^{-1} is assigned to the $[Sb_2F_{11}]^-$ anion. The remaining two IR active fundamentals ν_8 (νFe−C) and ν_9 (δC−Fe−C) have very low intensities so that the position of ν_8 is initially calculated from its combination bands $\nu_1 + \nu_8$ and $\nu_3 + \nu_8$, before the band is detected in the far-IR spectrum. Since the site symmetry of the cation is not strictly O_h, as discussed in the preceding section, the inactive T_{2u} fundamentals ν_{12} and ν_{13} are observed as weak bands in the IR spectrum of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$. The remaining inactive fundamental ν_5 (T_{1g}) is not seen, but its position can be obtained from combination bands. Finally for ν_6 a distinct manifestation of the Christiansen effect is noted in the observed band shape in both salts.

Of the six Raman active fundamentals of $[Fe(CO)_6]^{2+}$, ν_1, ν_3, and ν_{11} are highly intense, while ν_2 is of medium, and both ν_4 and ν_{10} are of very low intensities. Assignments of ν_2 and ν_4, which occur in a similar spectral region, are made with reference to the spectra for the isoelectronic species $[V(CO)_6]^-$,[37] $Cr(CO)_6$,[32,33] and $[Mn(CO)_6]^+$.[34] The exact order is determined by comparing the order and the ν_2/ν_4 intensity ratios in these species[32−34,37] and in $\nu_2 + \nu_6/\nu_4 + \nu_6$. The assignment is also supported by ab initio calculations.[85]

In addition to the bands listed in Table 3 for $[Fe(CO)_6]^{2+}$ and $[Fe(^{13}CO)_6]^{2+}$, a number of medium- to low-intensity bands are observed in the CO-stretching region which are attributed to mixed $^{12}CO-^{13}CO$ species. In the IR and Raman spectra of $[Fe(CO)_6]^{2+}$, bands of $[Fe(CO)_5(^{13}CO)]^{2+}$ are seen on account of the 1.1% natural abundance of ^{13}C. Likewise, in the spectra of $[Fe(^{13}CO)_6]^{2+}$ with an isotopic enrichment of $\sim$95%, bands attributable to $[Fe(CO)(^{13}CO)_5]^{2+}$ and $[Fe(CO)_2(^{13}CO)_4]^{2+}$ are observed. These bands are omitted from Table 3 but may be found together with a partial assignment in a complete listing of vibrational bands in the Supporting Information section.

Vibrational bands due to the anions are listed in the Experimental Section. The $[Sb_2F_{11}]^-$ anion has no symmetry (C_i), and hence, an extensive coincidence of IR and Raman bands is noted. A band observed at 492 cm^{-1} is assigned as asymmetric Sb−F−Sb stretch. For $[SbF_6]^-$ the symmetry in the crystal lattice departs from O_h and the mutual exclusion rule is no longer strictly valid. As a consequence the forbidden T_{2g} and T_{1u} vibrations are observed as weak shoulders in the far-IR spectrum. In addition to the fundamentals, a number of combination bands are found for $[SbF_6]^-$. A vibrational assignment for the $[SbF_6]^-$ anion is included in the Experimental Section.

The vibrational assignments for the $[Fe(CO)_6]^{2+}$ cation in $[Fe(CO)_6][Sb_2F_{11}]_2$ and in $[Fe(^{13}CO)_6][Sb_2F_{11}]_2$ are summarized in Table 4. The experimentally obtained wavenumbers for all 13 fundamentals are compared to the results of ab initio calculations[31] and to the data calculated in a normal coordinate analysis (NCA) to be discussed subsequently. There is excellent agreement between the NCA values and experimentally determined wavenumbers. Since ab initio calculations[31,38] involve the hypothetical gas-phase species $[Fe(CO)_6]_g^{2+}$, some small dis-

(85) Jonas, V. Personal communication.

Table 4. Vibrational Assignments of the Observed (obs.) and Calculated (Calc.) Wavenumbers ν [cm^{-1}] of the Fundamentals for [Fe(CO)₆]$^{2+}$ in [Fe(CO)₆][Sb₂F$_{11}$]₂ and [Fe(^{13}CO)₆][Sb₂F$_{11}$]₂

			[Fe(CO)₆][Sb₂F$_{11}$]₂		[Fe(^{13}CO)₆][Sb₂F$_{11}$]₂	
ν	sym. species	BP86/ECP2 calcd[a]	obs[b]	calcd[c]	obs[b]	calcd[c]
ν_1, νCO	A$_{1g}$	2221(−20)	2241.2	2241.5	2189.7	2189.3
ν_3, νCO	E$_g$	2188(−32)	2219.5	2219.9	2169.0	2168.9
ν_6, νCO	T$_{1u}$	2173(−31)	2204	2204	2154	2154
ν_7, δFeCO	T$_{1u}$	608(22)	586	586	571	571
ν_{10}, δFeCO	T$_{2g}$	508(7)	500.9	501	[482]	482
ν_{12}, δFeCO	T$_{2u}$	478(10)	468	468	452	452
ν_8, νFeC	T$_{1u}$	380(0)	380	380	374	375
ν_4, νFeC	E$_g$	355(−6)	361	361	355	355
ν_2, νFeC	A$_{1g}$	361(14)	347.1	347.7	342.7	342.1
ν_5, δFeCO	T$_{1g}$	338(2)	[336]	336	[326]	326
ν_{11}, δCFeC	T$_{1u}$	117(−53)	170	171	170	170
ν_9, δCFeC	T$_{2g}$	98(−40)	138	138	138	138
ν_{13}, δCFeC	T$_{2u}$	77(−37)	114	114	114	114

^{a} Values in parentheses are calculated ab initio minus observed wavenumbers, ref 31. ^{b} Values in square brackets are derived from overtones. ^{c} Using the force field presented in Table 5.

crepancies are expected and found. Crystal lattice effects are responsible for an increase of about 40 cm^{-1} for the observed C−Fe−C deformation modes ν_9, ν_{11}, and ν_{13}. The calculated values for the CO-stretching vibrations ν_1, ν_3, and ν_6 are lower by about 20−30 cm^{-1}, which is commonly noted for νCO obtained by ab initio methods.[31,38,39,86] Despite these and other small deviations, the calculated ab inito wavenumbers represent an excellent assignment aid for experimental data, since, for IR active vibrations, relative intensities are available as well.[31] Because the [Fe(CO)₆]$^{2+}$ cation in the solid state is only marginally affected by site symmetry perturbations or interionic interactions as discussed earlier, gaseous [Fe(CO)₆]$_g^{2+}$ provides a very good model and allows an excellent match of calculated and experimental wavenumbers.

As can be seen in Table 4, all 13 fundamentals of [Fe(CO)₆]$^{2+}$ are observed and assigned. The assignment is supported by ab initio[31] and NCA calculations. Among the salts with homoleptic metal carbonyl cations[25b] so far known, an equally extensive vibrational characterization has only been possible for [Au(CO)₂]-[Sb₂F$_{11}$].[87]

(d) Normal Coordinate Analysis (NCA) for [Fe(CO)₆]$^{2+}$. The molecular structure determinations of [Fe(CO)₆][SbF₆]₂ and [Fe(CO)₆][Sb₂F$_{11}$]₂, described in section b, provide two sets of nearly identical structural parameters for the cation [Fe(CO)₆]$^{2+}$ (see Table 2). For a normal coordinate analysis we have chosen the average values of 1.13 Å (d C−O) and 1.91 Å (d Fe−C). Based on a modified valence force field according to Wilson's F. G. matrix,[88] the normal coordinate analysis is carried out with the program MOLVIB.[89−91]

For the 13 atom molecular cation [Fe(CO)₆]$^{2+}$ in the symmetry point group O$_h$, the irreducible representations for vibrations are the following:

$$\Gamma_{vib} = 2\,A_{1g}\,(Ra) + 2\,E_g\,(Ra) + 1\,T_{1g}\,(-) + 4\,T_{1u}\,(IR) + 2\,T_{2g}\,(Ra) + 2\,T_{2u}\,(-)$$

Even though a different labeling of individual atoms is found in refs 32 and 33, the force constants are defined in a similar

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Table 5. Calculated Force Constants (10^2 N m^{-1}, Normalized on 1 Å Bond Length) of the GVFF for [Fe(CO)₆]$^{2+}$ and Cr(CO)₆ (g)

	[Fe(CO)₆]$^{2+}$	Cr(CO)$_6^a$
F_{CO}	19.698(55)	16.676(67)
F_{MC}	1.673(24)	2.029(67)
$F^{trans}_{CO,CO}$	0.063(59)	0.279 (67)
$F^{cis}_{CO,CO}$	0.047(34)	0.204(34)
$F_{CO,MC}$	0.367(48)	0.614(64)
$F^{trans}_{CO,MC}$	0.008(52)	−0.028(64)
$F^{cis}_{CO,MC}$	−0.022(29)	−0.052(28)
$F^{trans}_{MC,MC}$	0.462(24)	0.486(67)
$F^{cis}_{MC,MC}$	−0.025(3)	−0.019(3)
$F_{CO,\gamma} = F_{CO,\alpha'} - F_{CO,\alpha''}$	0	0
$F_{FeC,\gamma} = F_{FeC,\alpha'} - F_{FeC,\alpha''}$	0.035(30)	−0.150(84)
$F_{CO,\beta}$	0	0
$F_{FeC,\beta}$	−0.036(7)	−0.070(24)
$F_\alpha = F_a + F_{aa''} - 2F_{aa''''}$	1.202(91)	0.571(55)
$F_\gamma = F_a - F_{aa''}$	1.174(51)	0.519(64)
$F_{\gamma\gamma} = 2(F_{aa'} - F_{aa'''})$	0.2	0.172(64)
F_β	0.413(12)	0.511(20)
$F_{\beta\beta'}$	0.101(12)	0.126(20)
$F_{\beta\beta''}$	0.001(5)	0.000(8)
$F_{\beta\beta'''}$	0.029(7)	0.015(19)
$F_{\alpha\beta} = F_{\alpha\beta'} - F_{\alpha\beta''}$	0.036(7)	−0.087(4)
$F_{\gamma\beta'} = F_{\alpha\beta'} + F_{\alpha\beta''}$	0.045(11)	−0.109(27)
$F_{\gamma\beta''} = 2F_{\alpha\beta'''}$	0.022(12)	−0.033(27)

^{a} Vibrational data are taken from ref 32. Structural data are taken from ref 92.

manner. The force constants obtained are summarized in Table 5 and compared to those for Cr(CO)₆, which are also obtained here by use of the MOLVIB program. The structural parameters used for Cr(CO)₆ are 1.171 and 1.916 Å for d C−O and d Cr−C, respectively, taken from an electron diffraction study.[92] Vibrational data for solid Cr(CO)₆ are found in refs 32 and 33. As can be seen in Table 5, the decrease in π-back-bonding with increasing positive charge is reflected in a slight increase of F_{CO} and a concomitant even smaller decrease of F_{MC}. Far more pronounced, however, are differences in the interaction force constants $F_{CO/CO}$ or $F_{CO/MC}$, which are considerably smaller for [Fe(CO)₆]$^{2+}$ than for Cr(CO)₆, on account of decreased π-back-donation in the former. Unfortunately the molecular structure of [Mn(CO)₆]$^+$ is unknown and not enough vibrational data are available. Hence, a normal coordinate analysis cannot be extended to this species.

Not surprisingly, a F_{CO} value of 19.82 × 10^2 N m^{-1} for [Fe-(CO)₆]$^{2+}$, obtained by using the Cotton-Kraihanzel[93,94] ap-

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proximation, is in good agreement with the NCA value of $19.698(55) \times 10^2$ N m^{-1} for $[Fe(CO)_6]^{2+}$. On the other hand, approximated[93,94] interaction force constants of 0.21 and 0.06 $\times 10^2$ N m^{-1} for $F^{tr}_{CO/CO}$ and $F^{cis}_{CO/CO}$, respectively, agree much less with the NCA values of 0.063 and 0.047 $\times 10^2$ N m^{-1}. Reasonable agreement is found between the stretching force constants F_{CO} and F_{FeC} listed in Table 5 and values of 19.20 and 1.77×10^2 N m^{-1} from ab initio calculations[31] for gaseous $[Fe(CO)_6]^{2+}_{(g)}$. As the bond length data (section b) have shown, the strength of the C—O bond is slightly underestimated while the strength of the Fe—C bond appears to be overestimated in these calculations.[31]

In summary, the force constants for $[Fe(CO)_6]^{2+}$ and $Cr(CO)_6$, obtained from a normal coordinate analysis with the MO-LVIB[89–91] program and listed in Table 5, provide a more detailed and sensitive description of changes in π-back-bonding between both species than a comparison of bond length data or of CO-stretching frequencies can provide. In addition, vibrational wavenumbers for all 13 fundamentals of $[Fe(CO)_6]^{2+}$, recalculated from the force constants, produce an excellent match for the experimental data as seen in Table 4 and discussed in the preceding section.

(e) Magnetic Susceptibility Measurements of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$. The molecular structure determinations and the analysis of the vibrational spectra have shown that $[Fe(CO)_6]^{2+}$ is essentially octahedral in $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$ as well as in $[Fe(CO)_6][SbF_6]_2$. It follows that the complex cation must be diamagnetic with a low-spin $^1A_{1g}$ ground state. On the other hand, the oxidative carbonylation of $Fe(CO)_5$ has produced strongly paramagnetic products, when either Cl_2, AsF_5, or XeF_2 is used as an external oxidizing agent. The thermal decomposition of $[Fe(CO)_6][SbF_6]_2$ produces quantitatively $Fe[SbF_6]_2$, which has Fe^{2+} in a high spin configuration with a $^5T_{2g}$ octahedral ground state.[48] It is hence likely that variable amounts of $Fe[SbF_6]_2$, present in the product mixtures, are responsible for the observed paramagnetism. However, an unambiguous identification of $Fe[SbF_6]_2$ in the mixtures is not a trivial matter. The IR and Raman spectra of $Fe[SbF_6]_2$ are known,[28] but the reported band positions between 704–540 cm^{-1} and 285–273 cm^{-1} fall into extremely cluttered regions of the vibrational spectrum (see section c).

A more convincing identification of $Fe[SbF_6]_2$ is possible with the help of magnetic susceptibility measurements between 2 and 300 K. In Figure 7 the magnetic moments in this temperature range are shown for various preparations of "$[Fe(CO)_6]$-$[Sb_2F_{11}]_2$" with Cl_2, AsF_5, or XeF_2 as external oxidizing agents for $Fe(CO)_5$ and SbF_5 as reaction medium. They are compared to the magnetic moments of $Fe[SbF_6]_2$ in the same temperature range. The temperature dependence of magnetic moments shown in Figure 7 is typical for high spin Fe^{2+} with a $^5T_{2g}$ ground state and in an octahedral environment.[64,95] The magnetic moment of 5.40 μ_B at 300 K is comparable to a previously reported moment of 5.42 μ_B[48] and just slightly below the μ_{S+L} moment of 5.48 μ_B.[66] A detailed analysis of the magnetic behavior of $Fe[SbF_6]_2$ and related $M[SbF_6]_2$ salts, M = Cr, Cu, Pd, or Ag, is planned[96] at a later point, but it appears clear that all preparations of $[Fe(CO)_6][Sb_2F_{11}]_2$ have variable amounts of $Fe[SbF_6]_2$ as impurities, because a similar temperature dependence of μ is noted in all samples.

A sample of $[Fe(CO)_6][SbF_6]_2$ obtained from highly pure crystalline $[Fe(CO)_6][Sb_2F_{11}]_2$ as described in section a is
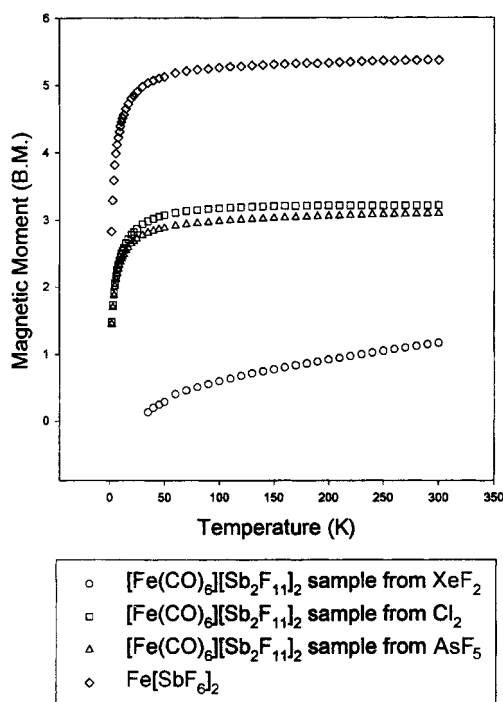
Figure 7. Magnetic moments of $Fe[SbF_6]_2$ and various preparations of $[Fe(CO)_6][Sb_2F_{11}]$ between 4 and 300 K.

essentially diamagnetic. A small μ^{eff}_{300} value is caused by less than 0.1% of $Fe[SbF_6]_2$ or may be due to temperature-independent paramagnetism.[95]

(f) The ^{57}Fe Mössbauer, ^{13}C NMR, and UV—Vis Spectra of $[Fe(CO)_6]^{2+}$. The results reported here complete the spectroscopic characterization of $[Fe(CO)_6]^{2+}$ by standard techniques and confirm the $^1A_{1g}$ ground state for iron. The ^{57}Fe Mössbauer spectrum of polycrystalline $[Fe(CO)_6][SbF_6]_2$ features a single line with an isomer shift δ of $-0.003(8)$ mm s^{-1} (rel. to α-Fe at R.T.) and a line width of 0.346(15) mm s^{-1}. The isomer shift is identical to the previously reported value for $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$[29] and comparable to δ values reported for the single line spectra of $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.042(5) mms^{-1}) and $(NH_4)_4$-$[Fe(CN)_6]$ ($-0.059(3)$ mms^{-1}).[97]

In the ^{13}C NMR spectrum of $[Fe(^{13}CO)_6]^{2+}$ in HF or DF with small amounts of SbF_5 added, a sharp single line at $\delta = 178.0$ ppm (line width 0.4 Hz) is seen. $J(^{13}C-^{57}Fe)$ is found to be 19.2 Hz. The value is slightly smaller than $J(^{13}C-^{57}Fe)$ found for $Fe(CO)_5$ (23.4 Hz). Since the coordination number of Fe in $[Fe(CO)_6]^{2+}$ is higher than in $Fe(CO)_5$,[98] its coupling constant is smaller and the ratio $23.4/19.2 \approx 6/5$ is reasonable.

Substantially higher $^1J(M-^{13}C)$ constants have been observed previously by us for $[Pt(CO)_4]^{2+}$ (1550 Hz)[99] and $[Hg(CO)_2]^{2+}$ (5220 Hz).[76] The higher values are explained by the lower coordination numbers and the substantially higher gyromagnetic ratios of the metals (Pt or Hg). Again the sharp line for $[Fe(CO)_6]^{2+}$ in solution and the observation of $^1J(^{13}C-^{57}Fe)$, which is experimentally demanding on account of the low natural abundance of ^{57}Fe (2.2%), are suggestive of a highly symmetrical $[Fe(CO)_6]^{2+}$ cation in solution.

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Table 6. Selected Structural and Spectroscopic Data for the Homoleptic Iron Carbonyls $[Fe(CO)_4]^{2-}$, $Fe(CO)_5$, and $[Fe(CO)_6]^{2+}$ [a]

species	$[Fe(CO)_4]^{2-}$	$Fe(CO)_5$	$[Fe(CO)_6]^{2+}$
(i) structure geometry	tetrahedral	trigonal bipyramidal	octahedral
bond length: Fe−C [Å]	1.762(17)[b]; 1.746(4)[c]	1.833(4)[d]; 1.806(5)[e]	1.908(7)[f]; 1.911(5)[g]
C−O [Å]	1.155(17)[b]; 1.175(5)[c]	1.145(3)[d]	1.108(9)[f]; 1.104(5)[g]
(ii) vibrational data			
νCO_{avg} [cm^{-1}]	1815[h]	2030[i]	2215
$f_{FeC} \times 10^2$ [N m^{-1}]		ax. 2.57[i] eq 2.64[i]	1.673(24)
$f_{CO} \times 10^2$ [N m^{-1}]	~13.30[h]	ax. 17.43[i] eq 16.47[i]	19.698(55)
(iii) ^{57}Fe Mössbauer data			
isomer shifts δ [mms^{-1}] rel. to α-Fe at 80 K	−0.18[j]	−0.09[j]	−0.003(6)
(iv) ^{13}C NMR data			
δ [ppm]		209.6[k]; 211.9[k]	178.0
$J(^{13}C-^{57}Fe)$ [Hz]	24.0[k]	23.2[k,l]	19.2

[a] Abbreviations: ax. = axial; eq. = equatorial. [b] [Na(crypt)₂][Fe(CO)₄], ref 45. [c] K₂[Fe(CO)₄], ref 45. [d] Fe−CO eq., ref 43. [e] Fe−CO ax., ref 43. [f] [Fe(CO)₆][SbF₆]₂. [g] [Fe(CO)₆][Sb₂F₁₁]₂. [h] Ref 105. [i] Ref 101. [j] Ref 102. [k] Ref 107. [l] Ref 98.

Unfortunately it has not been possible for us to record the UV−vis spectrum of $[Fe(CO)_6]^{2+}$ in HF−SbF₅ solution on account of experimental difficulties. The spectrum recorded on $[Fe(^{13}CO)_6][Sb_2F_{11}]_2$ crystals suspended in liquid SbF₅ features two broad bands at 31.2×10^3 and 38.3×10^3 cm^{-1}. The band positions are similar to those found for $[Fe(CN)_6]^{4-}$aq at 31.0×10^3 and 37.04×10^3 cm^{-1} [40] or for $Mo(CO)_6$ at 31.35 and 37.68×10^3 cm^{-1} and assigned to the d−d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. A ligand field analysis would produce values of 10 Dq = 34.6×10^3 cm^{-1} and $B \sim 487$ cm^{-1}, similar to the corresponding data for $[Fe(CN)_6]^{4-}$ of 33.8×10^3 cm^{-1} [40] and ~400 cm^{-1} [95] or $Cr(CO)_6$ at 34.15×10^3 cm^{-1}, respectively. There are three reasons which make such an assignment and the spectral analysis implausible for $[Fe(CO)_6]^{2+}$:

(i) The band assignment is not supported by reliably determined extinction coefficients, which should be ~10 L mol^{-1} cm^{-1} for spin allowed d−d transitions.[95]

(ii) The spectrum recorded by us looks very different from the one depicted in ref 95 for $[Fe(CN)_6]^{4-}$.

(iii) A 10 Dq value as high as 34.6×10^3 cm^{-1} would be nearly identical to 10 Dq reported for $Cr(CO)_6$,[40] while a B value of 487 cm^{-1} compared to a free ion B_0 value of 1060 cm^{-1} [95] would suggest extensive electron delocalization.

We hope that it will be possible to record a UV−vis spectrum of $[Fe(CO)_6]^{2+}$ in HF solution to assign both d−d and charge-transfer (CT) transitions in the future. However, this is not a trivial undertaking, due to the corrosive nature of the solvent.[24,73a] So far no other solvent has been found which will dissolve any of the two $[Fe(CO)_6]^{2+}$ salts without decomposition. Even then the assignment of d−d transitions will be a difficult task.[95]

Summary and Conclusions

The oxidative carbonylation of $Fe(CO)_5$ with XeF_2 allows the facile generation of superelectrophilic $[Fe(CO)_6]^{2+}$ in superacid media in high yield. The switch from liquid SbF₅ as reaction medium for carbonylation reactions[25b] to HF−SbF₅, reported here for the first time, produces $[Fe(CO)_6][Sb_2F_{11}]_2$ in very high purity and in the form of single crystals. The facile transformation of this salt to $[Fe(CO)_6][SbF_6]_2$ by washing with anhydrous HF provides the first thermally stable $[SbF_6]^-$ salt of a homoleptic superelectrophilic metal carbonyl cation.[25b] The cations in $[Fe(CO)_6][Sb_2F_{11}]_2$ and in $[Fe(CO)_6][SbF_6]_2$ have very similar average values for corresponding bond parameters and nearly identical band positions in their vibrational spectra. All 13 vibrational fundamentals of $[Fe(CO)_6]^{2+}$ are observed experimentally. The assignment is confirmed by the results of a normal coordinate analysis and supported by ab initio calculations.[31] A general valence force field for $[Fe(CO)_6]^{2+}$

allows a comparison to $Cr(CO)_6$.[32,33] The force constants, in particular interaction force constants, provide insights into bonding in the absence of significant π-back-donation for $[Fe(CO)_6]^{2+}$. Magnetic susceptibility measurements confirm the low spin configuration of Fe^{2+} in $[Fe(CO)_6]^{2+}$ with a $^1A_{1g}$ ground state in an octahedral environment and allow identification of $Fe[SbF_6]_2$[28,48] as the sole paramagnetic contaminant, which is formed in a competing reaction to the formation of $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$. The magnetic measurements are supported by the results of ^{57}Fe Mössbauer and ^{13}C NMR spectroscopy. Attempts to record the UV−vis spectrum of $[Fe(CO)_6]^{2+}$ are inconclusive, and a satisfactory band assignment is not possible at this time.

The principal structural and spectroscopic data for $[Fe(CO)_6]^{2+}$ are summarized in Table 6. They are compared to those for $Fe(CO)_5$ and $[Fe(CO)_4]^{2-}$, as far as these are available. The molecular structure of $Fe(CO)_5$ has been studied in the solid state as well as in the gas phase. An early X-ray diffraction study of solid $Fe(CO)_5$[100] suggested a trigonal bipyramidal structure with identical Fe−C (1.79(2) Å) and C−O (1.12(2) Å) bond distances for both the axial and equatorial CO groups. Electron diffraction data of gaseous $Fe(CO)_5$ listed in Table 6 show stronger Fe−C bonds for axial CO groups than for the equatorial ones[43] with the difference ΔFe−C 0.0204(55) Å,[44] while CO distances are identical in both studies.[43,44] As a consequence of the difference in Fe−C−O bond lengths, there are two different ^{13}C resonances in the ^{13}C NMR spectrum[98] and two distinctly different sets of internal valence stretching force constants[101] for $Fe(CO)_5$. As expected for a trigonal bipyramidal molecule, the ^{57}Fe Mössbauer spectrum[97,102] shows a quadrupole splitting of 2.57 mms^{-1} [97] whereas both $[Fe(CO)_4]^{2-}$ [102] and $[Fe(CO)_6]^{2+}$ have single line ^{57}Fe Mössbauer spectra.

On account of strong interionic interactions the $[Fe(CO)_4]^{2-}$ ion can be distorted from the expected tetrahedral symmetry, depending on the cation. For example, in $Na_2[Fe(CO)_4]\cdot1.5$(dioxane)[45] and to a lesser extent in $K_2[Fe(CO)_4]$,[45] the observed C−Fe−C bond angles depart significantly from the expected 109.5°. In $[Na(crypt)]_2[Fe(CO)_4]$, a regular $Fe(CO)_4$ tetrahedron is observed.[45] As seen in Table 6, there are some rather small differences in Fe−C and C−O bond lengths between the potassium and the $[Na(crypt)]^+$ salt.

The spectroscopic characterization of the $[Fe(CO)_4]^{2-}$ anion is rather cursory and incomplete. A limited number of IR bands

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of aqueous $[Fe(CO)_4]^{2-}$ are reported.[103] A Raman spectrum of an aqueous solution of $Na_2[Fe(CO)_4]$[104] appears to be incomplete according to a subsequent study on solid $Na_2[Fe(CO)_4]\cdot$ dioxane.[105] We have calculated an average CO-stretching frequency and an approximate stretching force constant on the basis of the latter study.[105] A much better situation is found for $Fe(CO)_5$, where the complete vibrational spectrum is known[33,106] and the potential force constants have been calculated.[101]

Also the ^{13}C chemical shift of $[Fe(CO)_4]^{2-}$ is not reported[98] and the coupling constant $J(^{13}C\text{-}^{57}Fe)$ listed in Table 6 is calculated and not experimentally determined.[107] Seemingly strong interionic interactions in the solid state[45] and solvent-dependent ion pair formation in solution[108] have limited the spectroscopic characterization of the supernucleophilic $[Fe(CO)_4]^{2-}$.[12]

For $[Fe(CO)_6]^{2+}$, secondary contacts to either $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ (see Figures 3 and 4) are less numerous and rather weak compared to $O\cdots K$ contacts in $K_2[Fe(CO)_4]$.[45] As a consequence any departures from octahedral symmetry for $[Fe(CO)_6]^{2+}$ are slight. Observed Fe–C distances for $[Fe(CO)_6]^{2+}$ are about 0.1 Å longer than the upper quartile value q_u of 1.801 Å from the Cambridge index[81] and may in fact be the longest distances recorded for iron carbonyls. Even for $Fe(CO)_5$,[43,44] the average Fe–C value is with 1.820(10) Å slightly longer than q_l,[81] while the average Fe–C distances in $K_2[Fe(CO)_4]$[45] and $[Na(crypt)]_2$-$[Fe(CO)_4]$[45] approximate q_l.[81] The reverse trend is found for C–O bond lengths in the three homoleptic iron carbonyl species.

The $\bar{\nu}CO_{avg}$ wavenumbers increase in steps of $\sim$200 cm^{-1} from $[Fe(CO)_4]^{2-}$ over $Fe(CO)_5$ to $[Fe(CO)_6]^{2+}$, while the force constants f_{CO} and f_{FeC}[101] appear to move in opposite directions. These observations are readily explained with decreasing π contributions and increasing σ contributions to Fe–CO bonding as the oxidation state of Fe moves from -2 to $+2$.

The data listed in Table 6 together with the results of ab initio calculations,[31,38] magnetic susceptibility measurements, and NCA and GVFF calculations presented here, indicate that $[Fe(CO)_6]^{2+}$, which is known only for a few years and studied only in the solid state, is equally well characterized as is $Fe(CO)_5$, which has been known well over a century.[5] This is a consequence of modern, widely available, physical, computational, spectroscopic, and diffraction techniques.

Supporting Information Available: Detailed crystallographic data, atomic coordinates, bond distances and bond angles, vibrational data, IR spectrum in the spectral range 2200–2900 cm^{-1}, UV–vis spectrum of $[Fe(^{13}CO)_6][Sb_2F_{11}]_2$ in suspended liquid SbF_5, structural drawings, internal coordinates of $[Fe(CO)_6]^{2+}$, and X-ray crystallographic files for $[Fe(CO)_6]$-$[Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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