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Synthesis and Spectroscopic Characterization of Hexakis(carbonyl)iron(II) Undecafluorodiantimonate(V), $[Fe(CO)_6][Sb_2F_{11}]_2$

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Oxidative carbonylation of $Fe(CO)_5$ in liquid SbF_5 and a CO atmosphere, with either AsF_5 or Cl_2 as external oxidizing agents, produces $[Fe(CO)_6][Sb_2F_{11}]_2$ in very high yield. The resulting off-white solid material is thermally stable (above 200 °C). The homoleptic carbonyl cation $[Fe(CO)_6]^{2+}$, the first of its type formed by a 3d-metal, is isostructural with $[Ru(CO)_6]^{2+}$ and $[Os(CO)_6]^{2+}$ which are obtained by reductive carbonylation of $M(SO_3F)_3$, M = Ru or Os. The stretching force constant of 19.82×10^2 N m^{-1} and $\bar{\nu}(CO)_{av}$ of 2215.5 cm^{-1} suggest significantly reduced π-back-bonding. The single line ^{57}Fe Mössbauer spectrum at $\delta = -0.001(6)$ mm s^{-1} relative to α-Fe is consistent with a regular octahedral structure and a $^1A_{1g}$ groundstate for $[Fe(CO)_6]^{2+}$. The possible existence of $[Fe(CO)_6]^{3+}$ formed by oxidation with Cl_2 is discussed.

Introduction

Dipositive homoleptic metal carbonyl cations for a 3d-series metal have so far remained unknown. We want to report at this time on the synthesis and the spectroscopic characterization of hexakis(carbonyl)iron(II) undecafluorodiantimonate(V), $[Fe(CO)_6][Sb_2F_{11}]_2$. The octahedral $[Fe(CO)_6]^{2+}$ is the first dipositive homoleptic carbonyl cation formed by a 3d-metal. The thermally stable (>200 °C) salt $[Fe(CO)_6][Sb_2F_{11}]_2$ is generated by a new synthetic approach, the oxidative carbonylation of $Fe(CO)_5$ in liquid antimony(V) fluoride, SbF_5. Its synthesis complements an earlier report[1] on the preparation of $[M(CO)_6][Sb_2F_{11}]_2$, M = Ru or Os, and allows a spectroscopic comparison of all three $[M(CO)_6]^{2+}$ cations formed by the group 8 metals iron, ruthenium, and osmium.

Results and Discussion

Even though the complex cyanide anion $[Fe(CN)_6]^{4-}$, found in $K_4[Fe(CN)_6]\cdot 3H_2O$, has been known for a very long time[2] and extensively studied,[3] the isoelectronic homoleptic carbonyl cation $[Fe(CO)_6]^{2+}$ has remained elusive, in spite of various attempts at its synthesis. Early claims of its formation by bromide abstraction from $Fe(CO)_4Br_2$ with the Lewis acid $AlBr_3$ at CO pressures of 300−400 atm[4] or by the postulated amine catalyzed disproportionation of $Fe(CO)_5$ to $[Fe(CO)_4]^{2-}$ and $[Fe(CO)_6]^{2+}$ [5] have subsequently been found in error.[6]

A recent, very promising approach, the reductive carbonylation in liquid SbF_5,[7] is found to be successful in the synthesis of the congeners $[M(CO)_6][Sb_2F_{11}]_2$, M = Ru or Os, from the corresponding fluorosulfates, $M(SO_3F)_3$, according to

$$2M(SO_3F)_3 + 16SbF_5 + 13CO \xrightarrow[25-70\ °C]{1\ \text{atm of CO, } SbF_5} 2[M(CO)_6][Sb_2F_{11}]_2 + CO_2 + S_2O_5F_2 + 4Sb_2F_9(SO_3F) \quad (1)$$

$$M = \text{Ru or Os}$$

But the method fails for FeX_3 (X = Cl or SO_3F), and polymeric $Fe[SbF_6]_2$, which has a layer structure,[8] is formed instead.

In order to avoid the formation of $Fe[SbF_6]_2$, the oxidative carbonylation of $Fe(CO)_5$ is attempted, with the assumption that most CO ligands will remain bound to Fe. It was found that by the use of AsF_5 as oxidizing agent, the reaction proceeds in a straightforward manner according to

$$Fe(CO)_5 + 5SbF_5 + AsF_5 + CO \xrightarrow[60-90\ °C]{1\ \text{atm of CO, } SbF_5} [Fe(CO)_6][Sb_2F_{11}]_2 + AsF_3\cdot SbF_5 \quad (2)$$

AsF_3 obtained as byproduct is complexed by SbF_5 to a white, nonvolatile solid, of the suggested composition $AsF_3\cdot SbF_5$.[9a] Removal from the reaction mixture requires repeated washing with liquid SO_2. The residue obtained after removal of all SO_2 from the liquid phase is identified by IR spectroscopy as $SO_2\cdot SbF_5$[9b] which suggests a displacement reaction during washing. The product $[Fe(CO)_6][Sb_2F_{11}]_2$ is an off-white, moisture-sensitive solid of surprising thermal stability, at least up to 200 °C. The composition of the isolated product is determined by the mass balance of the reaction and by microanalysis.

Interesting is the outcome of synthetic reactions with Cl_2 as external oxidizing agent. $[Fe(CO)_6]^{2+}$ is formed according to

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$$Fe(CO)_5 + Cl_2 + CO + 6SbF_5 \xrightarrow[60-80\ °C]{1\ atm\ of\ CO} [Fe(CO)_6][Sb_2F_{11}]_2 + 2SbF_4Cl \quad (3)$$

but in addition the mass balance of the reaction and a sharp IR band at 2256 cm^{-1}, whose intensity increases with increasing Cl_2 excess over the stoichiometrically required amount, suggest the formation of $[Fe(CO)_6]^{3+}$. Support comes from the recently reported $[Ir(CO)_6][Sb_2F_{11}]_3$[10] where the IR asymmetric CO stretch (f_{1u}) is observed at 2254 cm^{-1}. Attempts to obtain a pure sample of $[Fe(CO)_6][Sb_2F_{11}]_3$ and to characterize the cation $[Fe(CO)_6]^{3+}$ more fully are currently underway.

The oxidative carbonylation to generate homoleptic carbonyl cations has a precedent in the oxidation of gold by UF_6 in anhydrous HF and in the presence of CO to give $[Au(CO)_2][UF_6]$.[11] The oxidative carbonylation in liquid SbF_5, with the help of external oxidizing agents as described here, increases the potential use of antimony(V) fluoride in carbonylation reactions.

The IR and Raman spectra of $[Fe(CO)_6][Sb_2F_{11}]_2$ are shown in Figure 1, and all vibrational data of the cation are compared with the spectra of $[M(CO)_6]^{2+}$, M = Ru or Os,[1] in Table 1 together with the CO stretching force constants, f_{CO}. The bands of the $[Sb_2F_{11}]^-$ anion, not listed here, are very similar to those found in $[Hg(CO)_2][Sb_2F_{11}]_2$.[12] The tentative assignments are supported by the spectra of the ^{13}CO isotopomers.

It is more difficult to obtain the isotopomer $[Fe(^{13}CO)_6][Sb_2F_{11}]_2$ than $[M(^{13}CO)_6][Sb_2F_{11}]_2$, M = Ru or Os (see eq 1). The method chosen is the initial ^{13}CO enrichment of $Fe(CO)_5$ with $Na[BH_4]$ as exchange promotor[13] and the use of ^{13}CO in the subsequent oxidative carbonylation. In the resulting mixture of isotopomers, the ^{13}CO stretching modes of $[Fe(^{13}CO)_6]^{2+}$ are identified by comparison to the spectra of $[M(^{13}CO)_6]^{2+}$, M = Ru or Os.[1]

As can be seen in Table 1, vibrational spectra for the three $[M(CO)_6]^{2+}$ cations, M = Fe, Ru, or Os, are extremely similar in respect to band positions and intensities in particular in the CO stretching region. The three cations are evidently octahedral and the CO stretching force constant f_{CO} of 19.82 × 10^2 N m^{-1} for $[Fe(CO)_6]^{2+}$, obtained by the Cotton−Kraihanzel method,[14] suggests only insignificant metal to CO π-back-bonding.[15] The CO stretching force constant in $[Ru(CO)_6]^{2+}$ has the same value, while f_{CO} in $[Os(CO)_6]^{2+}$ is with 19.76 × 10^2 N m^{-1} slightly smaller.[1]

The observed decrease of $\delta(^{13}C)$ NMR chemical shifts from 179 ppm for $[Fe(CO)_6]^{2+}$ over 166 to 147 ppm for the corresponding Ru and Os hexacarbonyl cations is expected, since for the neutral hexacarbonyls $M(CO)_6$, M = Cr, Mo, or W, $\delta(^{13}C)$ decreases in a similar manner from 212 ppm over 204 to 192 ppm,[16] while the force constants f_{CO} for all three molecules are nearly identical.[17]

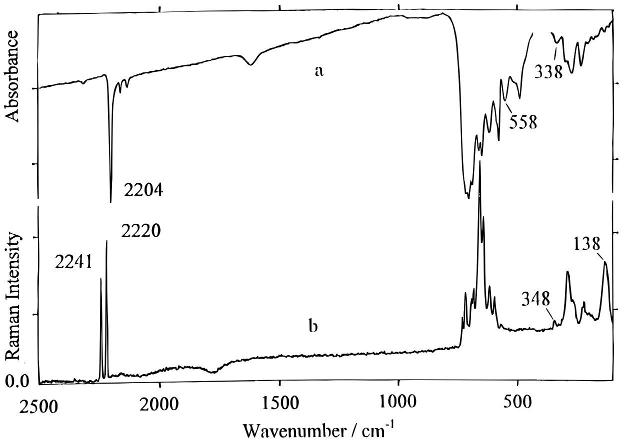

Figure 1. IR (a) and Raman (b) spectra of $[Fe(CO)_6][Sb_2F_{11}]_2$. Cation bands are marked.

Table 1. Vibrational Data in cm^{-1} and CO Stretching Force Constants f_{CO} in N m^{-1} × 10^2 for $[M(CO)_6][Sb_2F_{11}]_2$ (M = Fe, Ru, Os)

$[Fe(CO)_6][Sb_2F_{11}]_2$		$[Ru(CO)_6][Sb_2F_{11}]_2$		$[Os(CO)_6][Sb_2F_{11}]_2$		
IR intens	Raman intens	IR intens	Raman intens	IR intens	Raman intens	assignment[b]
	2241 s		2254[a] s		2259[a] s	ν_1 A_{1g} [M(CO)$_6$]
	2220 vs		2222[a] vs		2218[a] vs	ν_3 E_g [M(CO)$_6$]
2204 s		2199[a] s		2190[a] s		ν_6 F_{1u} [M(CO)$_6$]
	2190 m		2203[a] s		2206[a] s	ν_1' A_{1g} [M(^{13}CO)$_6$]
	2169 s		2172[a] vs		2166[a] vs	ν_3' E_g [M(^{13}CO)$_6$]
2155 s		2149[a] s		2141[a] s		ν_6' F_{1u} [M(^{13}CO)$_6$]
558 m		557 s		562 s		ν_7 F_{1u} [M(CO)$_6$]
	348 w		382 vw			ν_4 E_g [M(CO)$_6$]
338 w		336 m		346 m		ν_9 F_{1u} [M(CO)$_6$]
	138 m		131 s		132 s	ν_{11} F_{2g} [M(CO)$_6$]

Stretching Force Constants f_{CO}

M = Fe	M = Ru	M = Os
19.82	19.82	19.76

[a] Reference 1. [b] Numbering of fundamentals from ref 17.

The ^{57}Fe Mössbauer spectrum of $[Fe(CO)_6][Sb_2F_{11}]_2$ at 80 and 200 K shows a single sharp line (δ −0.001(6) mm s^{-1} relative to α-Fe at room temperature, Γ = 0.258(9) mm s^{-1} at 80 K). This observation suggests (a) the ground state of Fe^{II} is $^1A_{1g}$ corresponding to a $3d^6$ low spin configuration, (b) the environment around Fe is strictly octahedral, and (c) the electronic environment at the nucleus is slightly different from that of $K_4[Fe(CN)_6]\cdot 3H_2O$ which has an isomershift of −0.042 mm s^{-1}.[18]

Experimental Section

(a) Chemicals. Antimony(V) fluoride was obtained from Ato-Chem, North America, and purified by repeated distillation as described by us.[7,12] $Fe(CO)_5$ was obtained from BASF (purity not stated) and used without further purification. Cl_2 (Baker Chemiekalien Gross-Gerau) and SO_2 (Matheson, Europe) were obtained from commercial sources. Sulfur dioxide was dried over P_4O_{10}. AsF_5 was obtained by direct fluorination of elemental arsenic according to a literature method.[19] AsF_5 was stored in preconditioned metal cylinders.

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(b) Instrumentation and Equipment. Our equipment to obtain FT-IR, FT-Raman, and ^{13}C NMR-MAS spectra of solid samples has recently been described.[12] Also described is a two-part reaction flask, used in the purification of $[Fe(CO)_6][Sb_2F_{11}]_2$ by washing and decanting with liquid SO_2 to remove $AsF_3{\cdot}SbF_5$.[12]

(c) Synthetic Reactions. All synthetic reactions were carried out in glass reactors (about 60 mL volume) fitted with Teflon stem valves (Young, London, U.K.) and Teflon-coated stirring bars. Gaseous and volatile reagents and products were measured in a vacuum line of known volume. Pressure measurements were made with a Setra capacity manometer, Type 280E (Setra Instruments, Acton, MA). Solid materials were manipulated inside an evacuable box (Mecaplex, Grenchen, Switzerland) filled with N_2.

(i) Preparation of $[Fe(CO)_6][Sb_2F_{11}]_2$ with AsF_5. A reactor was charged with 122 mg (0.6 mmol) of $Fe(CO)_5$. After the reactor was cooled to liquid N_2 temperature, 106 mg (0.6 mmol) of AsF_5, 1.4 g (7.3 mmol) of SbF_5, and 1.9 mmol CO were added by transfer in vacuo. The reaction mixture was allowed to warm to room temperature and stirred. The initial yellow color vanished within 2 h. After the volatiles were removed in vacuo, 1.14 g of an off-white solid remained. The byproduct $AsF_3{\cdot}SbF_5$[9a] was removed by repeated washing with SO_2.

(ii) Preparation of $[Fe(CO)_6][Sb_2F_{11}]_2$ with Cl_2. A reactor was charged with 71 mg (0.36 mmol) of $Fe(CO)_5$. Without warming it to room temperature, 1.4 g (7.3 mmol) of SbF_5, 0.36 mmol of Cl_2, and 2.3 mmol of CO were added. After warming it to room temperature, the yellow reaction mixture was stirred for 1 h. The initial color had vanished. After all volatiles were removed, 0.46 g of an off-white solid remained. The weight was 12.9% higher than calculated for $[Fe(CO)_6][Sb_2F_{11}]_2$, possibly on account of incomplete SbF_5 removal.

$[Fe(CO)_6][Sb_2F_{11}]_2$ is a white, extremely moisture-sensitive solid, which does not decompose when heated in a sealed tube to 200 °C. Anal. Calcd for $C_6O_6F_{22}FeSb_4$: C, 6.4; Fe, 4.9; Sb, 43.1. Found: C, 5.4; Fe, 4.2; Sb, 42.7. The sample for analysis was prepared by method (i).

Conclusion

With the synthesis and spectroscopic characterization of thermally stable $[Fe(CO)_6][Sb_2F_{11}]_2$ reported here, the existence range of predominantly σ-bonded, homoleptic carbonyl cations extends now to the middle of the 3d-transition series. Previously only unipositive carbonyl cations are known for 3d metals. For Cu(I) (d^{10}) the existence of cations of the type $[Cu(CO)_n]^+$, with $n = 1, 2$, or 3, has been suggested.[20,21] The isoelectronic cation $[Mn(CO)_6]^+$, obtained as $[AlCl_4]^-$ salt, is known since 1961,[22a] but the $\bar{\nu}(CO)_{av}$ of 2121 cm^{-1} [22b] indicates some degree of π-back-donation compared to $\bar{\nu}(CO)_{av}$ of 2216 cm^{-1} for $[Fe(CO)_6]^{2+}$. The high thermal stability of $[Fe(CO)_6][Sb_2F_{11}]$ underscores once again the preeminent and unique role of $[Sb_2F_{11}]^-$ as a counteranion[12,23] for homoleptic metal carbonyl cations.

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