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Spectroscopic and Structural Characterization of Diphosphine and Diarsine Complexes of Iron(III) Iodide

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Introduction

Iron(III) iodide was recently[1] prepared by photolysis of a mixture of $Fe(CO)_4I_2$ and I_2 as a very unstable black solid of unknown structure. The tetrahedral tetraiodoferrate(III) anion $[FeI_4]^-$, originally prepared from $[FeCl_4]^-$ and liquid hydrogen iodide[2] and more recently from R_4NI, FeI_2, and I_2 under carefully controlled conditions,[3,4] and the tetramethylthiourea complex $[FeI_3\{SC(NMe_2)_2\}]$[5] appear to be the only isolated derivatives of iron(III) iodide. During recent studies of the effect of replacing chloride by iodide on the redox properties of various ruthenium and osmium complexes,[6] we examined some iron(II) complexes, including $[Fe(L\text{-}L)_2I_2]$ (L-L = o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, o-$C_6F_4(AsMe_2)_2$), by cyclic voltammetry and found that they underwent reversible 1-electron oxidations and that the products were stable in CH_2Cl_2 solution for some time. Here we report the isolation and structural characterization of the oxidation products which are the first examples of pseudooctahedral iron(III) iodide complexes.

Experimental Section

Physical measurements were made as described previously.[7] EXAFS data at the Fe K-edge were collected in transmission mode on station 7.1 at the Daresbury Synchrotron Source from samples diluted with BN. Details of the data collection and treatment are described elsewhere.[8,9] The Fe(III) samples were freshly prepared and stored below 0 °C before data collection. After data collection the samples were extracted from the BN with dry CH_2Cl_2, and their integrity was checked by recording their UV–visible spectra.

Preparation of *trans*-$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$. The Fe(II) complex was prepared from the reaction of $[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][FeCl_4]$ (0.5 g, 0.5 mmol) and an excess of LiI (0.75 g, 5 mmol) in acetone (40 cm^3) according to the literature route[10] (0.31 g, 0.35 mmol; 64%). Anal. Calcd for $[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$ ($C_{20}H_{32}As_4I_2Fe$): C, 27.2; H, 3.7. Found: C, 27.5; H, 3.7. The finely powdered iron(II) complex was suspended in 40% HBF_4 (15 cm^3) and concentrated HNO_3 (3 cm^3 total) added dropwise at 0 °C with vigorous stirring. The color of the suspension changed from yellow to brown, and the product was filtered off, washed with diethyl ether (2 × 5 cm^3), and dried *in vacuo*. Anal. Calcd for *trans*-$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ ($C_{20}H_{32}As_4BI_2F_4Fe$): C, 24.8; H, 3.3. Found: C, 24.4; H, 3.5. The other iron(III) complexes were prepared similarly. Anal. Calcd for $[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]BF_4$ ($C_{20}H_{32}BI_2F_4FeP_4$): C, 30.3; H, 4.1. Found: C, 30.7; H, 4.1. Calcd for *trans*-$[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]BF_4$ ($C_{20}H_{24}As_4BI_2F_{12}Fe$): C, 21.6; H, 2.2. Found: C, 21.2; H, 2.4.

Table 1. Data Recorded for $[Fe(L\text{-}L)_2I_2]BF_4$ Complexes

compound	$E_{max}/10^3\ cm^{-1}$ ($\epsilon_{mol}/dm^3\ mol^{-1}\ cm^{-1}$)[a]	$E°/V$[b]
$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$	12.9 (3900), 14.3 (530), 18.3 (670), 21.2 (2690)	+0.24
$[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]BF_4$	12.4 (1940), 15.2 (380) (sh), 18.2 (sh), 21.1 (1780)	+0.54
$[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]BF_4$	12.5 (2020), 14.1 (600), 14.9 (sh), 18.0 (380), 21.9 (1730)	+0.26

[a] Recorded in CH_2Cl_2. [b] Recorded in CH_2Cl_2 and standardized to the ferrocene/ferrocenium couple at +0.57 V.

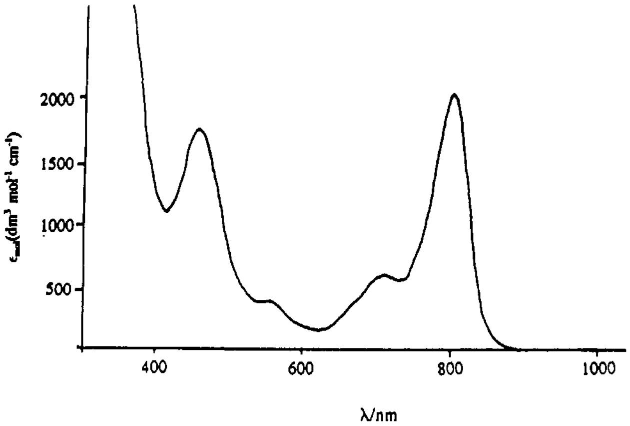

Figure 1. UV–visible spectrum of *trans*-$[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]BF_4$ in CH_2Cl_2 solution.

Results and Discussion

The pale yellow iron(II) complexes *trans*-$[Fe(L\text{-}L)_2I_2]$ suspended in 40% aqueous HBF_4 were easily oxidized by dropwise addition of concentrated HNO_3 at 0 °C to form dark brown *trans*-$[Fe(L\text{-}L)_2I_2]BF_4$. Cyclic voltammetry of the iron(II) complexes in CH_2Cl_2 revealed reversible Fe^{II}/Fe^{III} couples (Table 1) which occurred at potentials similar to those for the chloride and bromide analogues although, in contrast to these latter complexes, further reversible oxidation to Fe(IV) was not observed.[11] The solid iron(III) complexes decompose slowly at room temperature but can be kept at −10 °C in the dark for some weeks. The solutions of the complexes with L-L = o-$C_6H_4(PMe_2)_2$ and o-$C_6H_4(AsMe_2)_2$ in MeCN or CH_2Cl_2 decompose only slowly at ambient temperatures, but solutions of $[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]BF_4$ are completely decomposed in *ca.* 30 min. The analogous complex *trans*-$[Fe(Me_2PCH_2CH_2PMe_2)_2I_2]BF_4$ was obtained in solution but could not be isolated pure in the solid state; in contrast, attempts to oxidize the high-spin iron(II) complex[12] $[Fe\{o\text{-}C_6H_4(PPh_2)_2\}_2I_2]$ failed.

The UV–visible spectra of the iron(II) precursors show only very weak d–d transitions < *ca.* 25 000 cm^{-1},[13] but in contrast those of *trans*-$[Fe(L\text{-}L)_2I_2]BF_4$ consist of several intense features (Table 1, Figure 1). The spectra of *trans*-$[Fe(L\text{-}L)_2X_2]^+$ (X = Cl, Br) contain features at *ca.* 17 000 and *ca.* 25 000 cm^{-1} assigned[11,14] as P,As(σ) → Fe charge-transfer transitions (in order of increasing energy in local D_{4h} symmetry P,As(σ) → Fe(d_{xz},d_{yz}) and P,As(σ) → Fe(d_{z^2})). The feature at *ca.* 21 000 cm^{-1} in the spectra of the three iodo complexes may be similarly assigned as P,As(σ) → Fe(d_{z^2}). However, it is noticeable that the lowest energy absorption at *ca.* 13 000 cm^{-1} contains two distinct features; we assign one of these to the expected P,As(σ) → Fe(d_{xz},d_{yz}),

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Table 2. Fe K-Edge EXAFS and Relevant Crystallographic Data

compound	d(Fe–P/As)/Å[a]	$2\sigma^2$/Å^2 [b]	d(Fe–I)/Å	$2\sigma^2$/Å^2	FI[c]	R[d]
$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$	2.341(2)	0.008(02)	2.701(3)	0.011(05)	2.9	21.7
$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$	2.365(4)	0.010(04)	2.535(6)	0.011(09)	4.6	28.7
$[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]$	2.324(2)	0.008(02)	2.680(3)	0.010(05)	4.5	28.8
$[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]BF_4$	2.365(3)	0.008(03)	2.555(3)	0.007(04)	3.5	25.7
$[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$	2.222(3)	0.015(06)	2.665(6)	0.020(06)	8.7	36.2
$[Fe\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]BF_4$	2.292(4)	0.006(06)	2.571(6)	0.013(1)	9.6	32.1
$[Fe(Me_2PCH_2CH_2PMe_2)_2Cl_2]$[e]	2.241(1), 2.230(1)					
$[Fe\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]BF_4$[f]	2.292(1), 2.295(1)					
$[Fe(Et_2PCH_2CH_2PEt_2)_2I_2]$[g]	2.295(1), 2.323(1)		2.706(1)			
$[NEt_4][FeI_4]$[h]			2.531(3)			
$[FeI_3\{SC(NMe_2)_2\}]$[i]			2.553(1), 2.530(1), 2.537(1)			
$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2NCS(NO)]BPh_4$[j]	2.359(2)–2.379(2)					

[a] Standard deviations in parentheses. Note that systematic errors in bond distances arising from data collection and analysis procedures are *ca.* ±0.02 Å for well-defined shells.[21] [b] Debye–Waller factor. [c] Fit index defined as $\sum_i[(\chi^T - \chi^E)k_i^3]^2$. [d] R factors defined as $[\int(\chi^T - \chi^E)k^3\,dk/\int\chi^E k^3\,dk] \times 100\%$. The relatively high FI's and R factors are a reflection of the features >3 Å in the Fourier transforms which correspond to carbon shells in the ligand. These cannot be adequately modeled. Fourier filtered data with a window 1–3.5 Å reduce the R factors by 10–15%. [e] Reference 19. [f] Reference 18. [g] Reference 12. [h] Reference 4. [i] Reference 5. [j] Reference 20.

while the second is likely on optical electronegativity grounds[15] to be $I(\pi) \rightarrow Fe(d_{xz},d_{yz})$. We note that the spectrum of *trans*-$[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ is similar to that of the product of the reaction of $[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ with CHI_3, studied *in situ* by Zink *et al.*,[14] although in that study the complex was not isolated.

The very characteristic form of the UV–visible spectra of the iron(III) iodo complexes strongly resembles those of *trans*-$[M(L\text{-}L)_2I_2]^+$ (M = Ru, Os)[6] and confirms the *trans* 6-coordinate structures (D_{2h}). Attempts to obtain a single-crystal X-ray structure of one of these complexes have been unsuccessful,[16] but the local iron environment has been established via Fe K-edge EXAFS (extended X-ray absorption fine structure) studies. The Fe K-edge XANES lack the intense 1s → 3d electronic transition which would be expected for a tetrahedral complex, providing further support for the presence of 6-coordinate iron. For the diarsine complexes a good fit of the EXAFS data was achieved for a two-shell model of four arsenics and two iodines, and this was satisfactorily refined. It proved more difficult to obtain a good fit for the diphosphine complex data, which was at least in part due to the presence of features in the Fourier transform in the region 3–5 Å which tended to partially overlap with the Fe–I shell. These features are due to carbon shells from both the methyl groups and the aromatic carbons, but because of the spread of Fe···C distances[17] and multiple scattering effects, these cannot be satisfactorily modeled. The best fits for the two-shell models and the resulting parameters are listed in Table 2, and Figure 2 shows a typical example. Table 2 also contains relevant X-ray crystallographic data for comparison, from which it can be seen that the Fe–P distances for both the Fe(II) and Fe(III) complexes compare well with those in related compounds.[12,18,19] The Fe–I distances in the Fe(II) compounds can be compared with that[12] in *trans*-$[Fe(Et_2PCH_2CH_2PEt_2)_2I_2]$ (2.706(1) Å), while those in the Fe(III) complexes are on average slightly longer than those found in $[FeI_4]^-$ or $[FeI_3\{SC(NMe_2)_2\}]$, the effect expected with the increase in coordination number of the iron. Most significantly the Fe–I distances shorten as the oxidation state increases from Fe(II) to Fe(III), while the Fe–P/As distances increase slightly, exactly the same trends as observed for the corresponding chlorides.[11,18] This probably reflects stronger interaction of the harder Fe(III) center with the halide and weaker interaction with the P/As donors compared to those involving the softer Fe(II) center.[11]

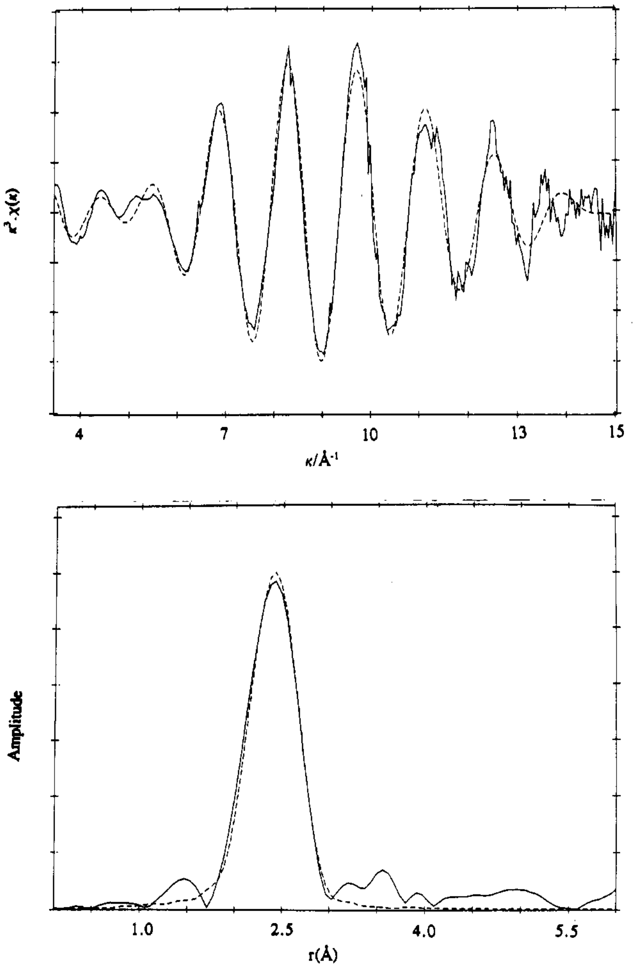

Figure 2. Top: Background-subtracted Fe K-Edge EXAFS of *trans*-$[Fe\{o\text{-}C_6F_4(AsMe_2)_2\}_2I_2]BF_4$. Bottom: Corresponding Fourier transform, phase-shift-corrected for arsenic.

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(17) The X-ray structure of $[Fe\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]BF_4$[18] revealed $Fe\cdots C_{Me}$ contacts at 3.48–3.54 Å and $Fe\cdots C_{ipso}$ at *ca* 3.33 Å.

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