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Ferric Iodide as a Nonexistent Compound

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"Nonexistent" inorganic compounds have been precluded on thermodynamic grounds or by unfavorable reaction pathways and conditions.[1] Ferric iodide is one such common example: "... iron(III) is too strong an oxidizing agent to coexist with such a good reducing agent as I^-..."[2] We have recently shown how this thermodynamic limitation (in water) can be overcome by carrying out the synthesis of ferric iodide in wholly nonaqueous media with diiodotetracarbonyliron(II),[3] which is soluble in even such hydrocarbon solvents as *n*-hexane, i.e.[4]

$$(OC)_4FeI_2 + \tfrac{1}{2}I_2 \xrightarrow[C_6H_{14}]{h\nu} FeI_3 + 4CO \tag{1}$$

The photochemical synthesis in eq 1 is based on the analogous transformation of iron pentacarbonyl with dibromine to anhydrous ferric bromide via the intermediacy of the hydrocarbon-soluble dibromotetracarbonyliron(II). Ferric bromide produced under these aprotic conditions shows an unusually high catalytic activity.[5] Although alternative methods are available for the synthesis of pure ferric bromide,[6] the oxidative photodecarbonylation of diiodotetracarbonyliron(II) according to eq 1 (with I = Br) appears to be a preparative method that is uniquely suited for the metastable ferric iodide. Unfortunately our previous attempts at the structural characterization of ferric iodide were limited by the low photochemical conversions arising from the competing induced decomposition, i.e.

$$FeI_3 \xrightarrow{h\nu} FeI_2 + \tfrac{1}{2}I_2 \tag{2}$$

As such, it was left for us to (a) improve the synthesis and collect sufficient amounts of material for a complete elemental analysis of pure FeI_3, (b) establish its identity as ferric iodide by chemical means, (c) compare its spectroscopic properties with the related iron(III) halides, and (d) examine the iron(III) content of FeI_3 by Mössbauer spectroscopy. The successful attainment of the first three objectives (a–c) and the partial resolution of the fourth (d) are reported herein. Although the Mössbauer results were not wholly satisfactory (due to the extreme metastability of ferric iodide), we believe they are sufficiently informative to warrant the solicitation of further studies.

Results and Discussion

Synthesis and Elemental Analysis of FeI_3. Iron pentacarbonyl was converted in situ to diiodotetracarbonyliron(II)[3] by treatment with excess diiodine in rigorously dried *n*-hexane under an argon atmosphere. Careful irradiation of the solution at −20 °C with actinic light (for details see Experimental Section) led to the slow evolution of carbon monoxide and the deposition of a black film. The extremely hygroscopic black solid was sparingly soluble only in dichloromethane to afford a dark purple solution (vide infra), but its exposure to donor solvents such as tetrahydrofuran, acetonitrile, and pyridine (as well as water) spontaneously led to ferrous iodide and diiodine with the same stoichiometry as that given in eq 2. The submission of the metastable sample to several commercial laboratories for elemental analysis led to widely erratic results. Accordingly, we carried out the iron and iodine analysis immediately after synthesis (see Experimental Section). Since the elemental analysis was sufficient to establish its stoichiometric purity, the black binary compound containing only iron and iodine will be referred to hereafter simply as FeI_3.

Quantitative Conversion of FeI_3 to Tetraiodoferrate(II). The direct conversion of FeI_3 to the known[9] tetraiodoferrate(III) with added iodide, i.e.

$$FeI_3 + I^- \rightarrow FeI_4^- \tag{3}$$

constitutes the simple, least ambiguous chemical probe for its identification as ferric iodide. In order to carry out this transformation quantitatively, FeI_3 was prepared directly in a spectrophotometric cuvette from a dilute solution of iron pentacarbonyl and excess diiodine in hexane.[10] To avoid any loss by isolation, the black film was washed with hexane in the dark and then dissolved in situ with rigorously purified dichloromethane under an argon atmosphere. The labile deep purple solution of FeI_3 reacted rapidly (on mixing) with successive aliquots of tetra-*n*-butylammonium iodide dissolved in dichloromethane until 1 equiv of iodide was added (relative to the $Fe(CO)_5$ initially charged). The spectral change accompanying the titration of FeI_3 with iodide is illustrated in Figure 1A. For comparison, the absorption spectrum of an authentic sample of tetraiodoferrate(III), prepared as the tetra-*n*-butylammonium salt,[9] is shown in Figure 1B. Importantly, the well-resolved absorption band at $\lambda_{max} = 698$ ($\epsilon_{max} = 4400$ M^{-1} cm^{-1}) was used to establish the quantitative transformation of FeI_3 according to eq 3.

Ligand Exchange of FeI_3 to Ferric Chloride. Metathesis of chloro for iodo ligands in FeI_3 to generate ferric chloride represents an alternative chemical probe for the identification of ferric iodide. Indeed FeI_3, like ferric bromide, exhibited unusual reactivity in various types of substitutional processes.[5] For example, the dark purple solution of freshly prepared FeI_3 in dichloromethane was immediately bleached upon exposure to different alkyl chlorides (RCl) such as the *t*-butyl, 1-adamantyl, and 2-norbornyl derivatives. The absorption spectrum of the resultant pale yellow solution coincided with that of an authentic sample of ferric chloride (vide infra),[4] and quantitative gas chromatographic analysis established the reversible formation of the corresponding organic iodides according to the stoichiometry

$$FeI_3 + 3RCl \rightleftarrows FeCl_3 + 3RI \tag{4}$$

It is important to emphasize that the use of the nonionic alkyl chlorides in eq 4 precluded the formation of tetrachloroferrate(III) and related complex anions that are commonly encountered during the metathesis of iron(III) complexes with alkali-metal chlorides.

Spectral Relationship of FeI_3 to Tetraiodoferrate(III) and the Bromo/Chloro Analogues. The absorption spectra of FeI_3 and FeI_4^- in Figure 1 bear a consistent relationship to those of their bromo and chloro analogues. For example, in the series of tetrahedral ferrates $FeCl_4^-$, $FeBr_4^-$, and FeI_4^- (that have all been

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(10) High conversions were possible in dilute solutions containing excess diiodine (vide infra).

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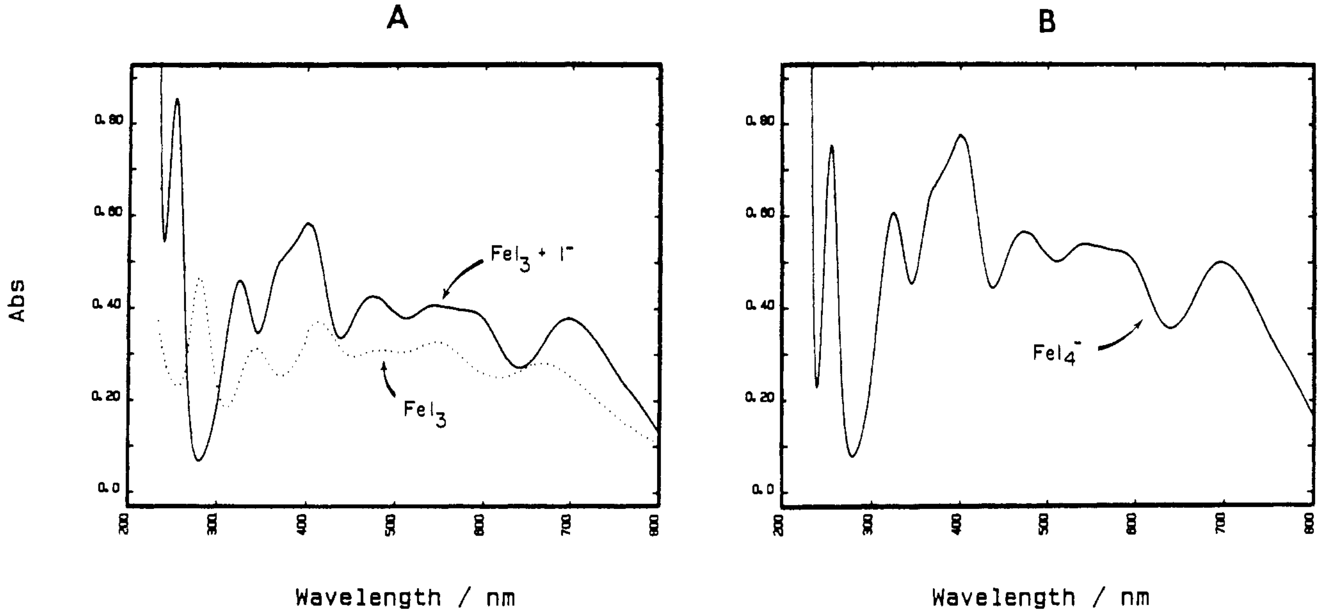

Figure 1. Absorption spectra of iodoiron(III) species in dichloromethane solution: (A) FeI_3 (lower) and FeI_4^- (upper) from the addition of $Bu_4N^+I^-$; (B) $Bu_4N^+FeI_4^-$ prepared according to Pohl and Saak.[9]

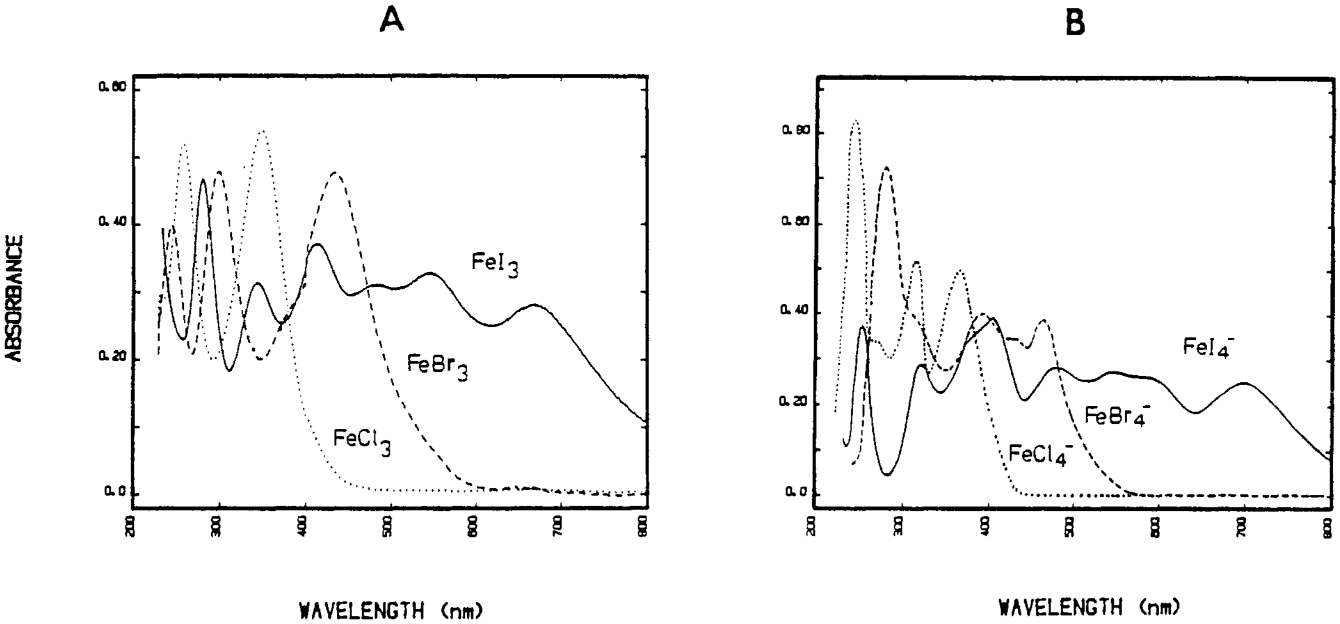

Figure 2. Comparative absorption spectra of (A) ferric chloride (···), ferric bromide (- - -), and ferric iodide (—) and (B) tetrachloroferrate (···), tetrabromoferrate (- - -), and and tetraiodoferrate (—) in $\sim 10^{-4}$ M dichloromethane.

structurally characterized by X-ray crystallography[11-13]), the absorption bands listed in Table I show a progressive red shift in the LMCT bands in accord with the increasing donor strengths of the ligand.[14] Similarly in the series of trihaloiron(III) complexes $FeCl_3$, $FeBr_3$, and FeI_3, the same progression of bathochromic shifts occurs, together with an increasing number of absorption bands.[15,16] Moreover, the pairs of haloiron(III) species $FeCl_3/FeCl_4^-$, $FeBr_3/FeBr_4^-$, and FeI_3/FeI_4^- are consistently related to each other, the charge-transfer bands of the ferrates being always red-shifted relative to those of the uncharged species. In other words, the generally red-shifted absorption spectrum of FeI_3, which follows from the spectral progression of $FeBr_3$ and $FeCl_3$ in Figure 2A, is strikingly akin to that of the known ferrate

Table I. Electronic (UV–Vis) Absorption Bands of Haloiron(III) Species[a]

	absorptions, λ (ε)[b]
$FeCl_3$[c]	257 (5650), 347 (5700)
$FeCl_4^-$[d]	243 (11 900), [272], 314 (7600), 364 (7350)
$FeBr_3$[e]	244 (3500), 299 (4200), 432 (3850)
$FeBr_4^-$[d]	281 (10 500), [317], 392 (5960), [424], 472 (5800)
FeI_3	281 (5460), 344 (3700), 416 (4390), 482 (3650), 552 (3870), 676 (3300)
FeI_4^-[f]	254 (7200), 325 (5450), [370], 400 (7360), 484 (5100), 536 (4740), 582 (4650), 698 (4400)

[a] In dichloromethane solution. [b] In units of nm (M^{-1} cm^{-1}) with shoulders in brackets. [c] Compare with ref 15. [d] From ref 14b. [e] Compare with ref 16. [f] Compare with ref 13a.

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FeI_4^- in its relationship to the analogues $FeBr_4^-$ and $FeCl_4^-$ in Figure 2B. Although the assignments of these absorption bands are not yet complete, the spectral similarities in the two series are unmistakable, and they strongly support the formulation of FeI_3 as ferric iodide.

It is likely that ferric chloride and ferric bromide are present in solution primarily as the halo-bridged dimers, much as they exist in the vapor phase.[16-18] If so, the spectral extension to FeI_3 suggests that ferric iodide also exists in solution as a μ-iodo species. Thus coordinative saturation that is achieved with a pair of iodo ligands in $(FeI_3)_2$ is akin to that extant in FeI_4^-, as also exhibited in their spectral similarity. Indeed, the pervasiveness of this structural interrelationship among the iron(III) halides may be responsible for the general appearance of the spectra in Figure 2A relative to those in Figure 2B.

Metastability of FeI_3. Exposure of FeI_3, either as a thin black film or in dichloromethane solution, to small amounts of moisture or to light (even diffuse room light) led to ferrous iodide (insoluble brown powder) and 0.5 mol of diiodine (purple vapors). Quantitative analysis was effected by the separation of all the volatile material from the reaction mixture (photolysate) by vacuum transfer into a liquid-nitrogen trap. The amount of diiodine was determined spectrophotometrically by its distinctive absorption band at $\lambda_{max} = 504$ nm ($\epsilon_{max} = 800$ M^{-1} cm^{-1}).[19] The ferrous iodide was quantitatively assayed by the addition of an aqueous solution of 1,10-phenanthroline directly to the residue followed by the spectrophotometric determination of $Fe(phen)_3^{2+}$ (vide supra).[20] The quantum yield of $\Phi = 0.32$ was established by ferrioxalate actinometry[21] for the photolytic decomposition of FeI_3 in dichloromethane with monochromatic light at $\lambda = 405$ nm. The decrease in the photoefficiency to $\Phi = 0.08$ in the presence of a 10-fold excess of diiodine was consistent with homolytic decomposition of FeI_3, since diiodine is known to be an effective chain-transfer agent in aprotic media,[22,23] e.g.

$$FeI_3 \rightleftharpoons [FeI_2] + I^\bullet \tag{5}$$

$$[FeI_2] + I_2 \rightarrow FeI_3 + I^\bullet \tag{6}$$

$$2I^\bullet \rightarrow I_2 \tag{7}$$

where the inclusion in brackets denotes monomeric iodoiron(II) species. Indeed the rapid decomposition accompanying the introduction of dry dioxygen to a dichloromethane solution of FeI_3 is consistent with the shift in the equilibrium (eq 5) by the facile oxidation of $[FeI_2]$. The latter was observed as fine light brown particles of (uncharacterized) oxoiron(III) species together with diiodine ($\lambda_{max} = 504$ nm). Otherwise, we find it difficult to account for the high sensitivity of such an already oxidized iodoiron(III) species to dioxygen, even in the solid state at −180 °C (see Experimental Section). By contrast, the rate of decomposition of tetraiodoferrate(III) under the same conditions was significantly slower, the intensity of the unique absorption band at $\lambda = 698$ nm (Figure 1B) decreasing by only 30% over the course of 15 h. Likewise, the brown ferrous iodide (polymeric) solid was largely unaffected by dioxygen.

The Mössbauer Effect of FeI_3. Although the partial decomposition of the highly labile FeI_3 was unavoidable,[24] the experimental Mössbauer spectrum at 4 K was successfully deconvoluted to yield iodoiron(III) as the principal spectral component (45%) consisting of six hyperfine lines with a 3:2:1:1:2:3 intensity ratio (see Experimental Section). The Mössbauer parameters of $\delta = 0.31$ mm s^{-1} and $H_{hf} = 326$ kOe are compared in Table II with those previously reported for FeF_3, $FeCl_3$, and $FeBr_3$. Moreover, the comparison with tetraiodoferrate(III),[13] the only known binary iodide of iron(III), is particularly instructive since the electronic state of high-spin iron(III) in FeI_4^- has been characterized by Mössbauer spectroscopy, with the isomer shift of $\delta = 0.31$ mm s^{-1} and hyperfine splitting by an internal magnetic field of $H_{hf} = 343$ kOe for the tetraethylammonium salt.[25] The experimental spectrum of $Et_4N^+FeI_4^-$ shown in Figure 3 (lower) confirms these Mössbauer parameters. It is noteworthy that the latter are strikingly akin to the Mössbauer parameters for the principal constituent of FeI_3 as listed in Table II. Furthermore, both sets of Mössbauer parameters are wholly consistent with those evaluated from the trends established for the analogous series of tetrahaloferrate(III) and trihaloiron(III) with fluoro, chloro, and bromo ligands in Table II.[26-34] Indeed, their strong similarity is underscored by the juxtaposition of the Mössbauer spectra in Figure 3. The Mössbauer parameters for the principal component of FeI_3 point to a high-spin tetrahedral iodoiron(III). The latter

Table II. Mössbauer Parameters of Binary Iron Halides

compd	temp, K	δ vs α-Fe, mm s^{-1}	eQ, mm s^{-1}	H_{hf}, kOe	T_N, K	ref
FeF_2	4.2	1.48	2.85	329	78.12	26
$FeCl_2$	4.2	1.093	1.21	4		27
$FeBr_2$	5.0	1.12	1.09	29.6	11	27, 28
FeI_2	4.2	1.044	0.962	74	10	27
$(Me_4N)_2FeCl_4$	4.2	0.90	3.27			29
$(Et_4N)_2FeBr_4$	4.2	0.97	3.23			29
FeF_3	4.2	0.489	0.044	618.1	363	30
$FeCl_3$	4.2	0.461	0.04	470[a]	15	27, 31, 32
$FeBr_3$	78	0.55				31
FeI_3	4.2	0.310	0.06	326	~12	this work
Et_4NFeCl_4	1.1	0.205	0	470	3.0	25, 33, 34
Et_4NFeBr_4	1.3	0.27	0	420	3.9	25, 33, 34
Et_4NFeI_4	4.2	0.31		343	24	25
Et_4NFeI_4	4.2	0.315	<0.02	347		this work
Bu_4NFeI_4	1.4	0.305		341	11	25

[a] Average of the literature values.

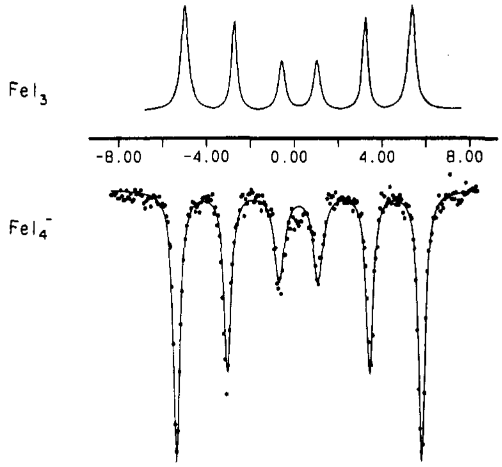

Figure 3. Comparison of the Mössbauer spectra of FeI_4^- (lower) and FeI_3 (upper, phase I).

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Table III. Mössbauer Parameters of FeI_3[a]

temp, K	phase[b]	δ vs FeRh,[c] mm s^{-1}	δ vs α-Fe, mm s^{-1}	eQ,[d] mm s^{-1}	W,[e] mm s^{-1}	H_{hf},[f] kOe
4.2	I	0.200 (8)	0.310 (8)	<0.06	0.260 (8)	326 (5)
	II	1.14 (1)	1.25 (1)	2.86 (1)	0.50 (1)	
	III	−0.13 (1)	−0.02 (1)	0.33 (1)	0.50 (1)	
77	I	0.189 (8)	0.300 (8)	0.07 (1)	0.45 (1)	
	II	1.11 (2)	1.22 (2)	2.80 (3)	0.55 (1)	
	III	−0.15 (2)	−0.04 (2)	0.37 (3)	0.35 (1)	

[a] By deconvolution of the experimental spectra. [b] See text. [c] Isomer shift relative to $^{57}Co(Rh)$. [d] Quadrupole splitting. [e] Line width. [f] Magnetic hyperfine field.

is supported by the measurement of the magnetic susceptibility of FeI_3, which yields after correction (see Experimental Section) $\mu_{eff} = 5.9\ \mu_B$, in agreement with the $^6S_{5/2}$ state. The tetrahedral structure for ferric iodide can derive from the participation of iodide as a bridging ligand in dimeric and/or polymeric units.[35,37] The decreased magnitude of $H_{hf} = 326$ kOe in FeI_3 relative to those in the halide analogues FeF_3 (618 kOe) and $FeCl_3$ (470 kOe) may be a reflection of an increased covalency in the iron–halogen bond, similar to the trend observed in the corresponding series of tetrahaloferrates.[25] Further discussion of the Mössbauer spectrum of FeI_3, such as the interesting antiferromagnetic → paramagnetic phase transition observed at 12 K, is premature, and Mössbauer facilities at 4 K are clearly required to be immediately at hand for these critical measurements.

Experimental Section

Materials. Iron pentacarbonyl (Aldrich) was redistilled in vacuo and stored in a Schlenk flask under an argon atmosphere at −20 °C. Diiodine (Mallinckrodt, reagent grade) was sublimed twice in vacuo. Hexane (Fisher, reagent grade) was repeatedly treated with concentrated sulfuric acid, washed with water, and distilled from sodium under an argon atmosphere. Dichloromethane (Fisher, reagent grade) was treated with sulfuric acid, washed with water, and distilled from P_2O_5 under an argon atmosphere. Tetraiodoferrate(III) was synthesized as the tetraethylammonium salt according to the procedure of Pohl and Saak.[9]

Synthesis of FeI_3. A scrupulously cleaned, 1-L round-bottom Schlenk flask (equipped with a Teflon stopcock and sleeves to obviate contamination by grease) was flame-dried under vacuum. Dry hexane (120 mL) and diiodine (100 mg, 0.39 mmol) were introduced under a reverse flow of argon. Upon the complete dissolution of diiodine, $Fe(CO)_5$ (15 μL, 0.11 mmol) was added in the dark under a reverse flow of argon. The mixture was stirred until homogeneous (2–3 min), and the flask was then kept in the dark for an additional 1 h with occasional swirling to allow the formation of $Fe(CO)_4I_2$ to be completed.[3] The flask was then immersed in a CCl_4 bath (maintained at −20 °C and contained in an unsilvered Dewar flask) to 1 in. above the liquid level. The homogeneous solution of $Fe(CO)_4I_2$ and diiodine was weakly irradiated with the diffuse output of a 50-W fluorescent light held approximately 1 m above the surface. The initially light red solution gradually darkened and deposited an almost black solid as the carbon monoxide was slowly liberated. Irradiation for 2.5 h was considered optimum, since the prolonged actinic exposure led to decomposition according to eq 2. The mother liquor was removed with the aid of a Teflon cannula, and the black, extremely hygroscopic deposit was washed with hexane in the dark under an argon atmosphere. After the contents were dried in vacuo, the flask was transferred to a drybox (Vacuum Atmospheres Model MO-41 with <5 ppm O_2) and the thin black deposit laboriously removed from the flask wall. Typically, 10–15 mg of FeI_3 was obtained by this procedure. All attempts to achieve higher conversions invariably led to material of significantly lower quality that contained increased amounts of ferrous iodide (and diiodine). Since the submission of the unstable sample to several commercial laboratories for elemental analysis led to widely erratic results, we carried out the iron and iodine analysis of a 50-mg sample (combined from four separate runs) by dissolution in 25 mL of 0.03 M ceric sulfate in 2 N sulfuric acid. The liberated diiodine was repeatedly extracted into CCl_4, and iodometric titration was carried out with a standard solution of $Na_2S_2O_3$.[7a] The pale yellow aqueous solution was reduced with zinc amalgam[7b] and the reduced iron(II) determined spectrophotometrically after conversion to the tris(1,10-phenanthroline) complex with $\epsilon = 1.11 \times 10^4\ M^{-1}\ cm^{-1}$ at 510 nm.[8] Anal. Calcd for FeI_3: I, 87.12; Fe, 12.88. Found: I, 86.5; Fe, 13.2. Although the dark powder of FeI_3 was partially soluble in dichloromethane, the attempts to grow single crystals have been uniformly unsuccessful since further manipulations generally led to enhanced decomposition (see eq 2).

Measurement of the Mössbauer Effect of FeI_3. The Mössbauer spectra were obtained on a Halder constant-acceleration spectrometer in conjunction with a multichannel analyzer operating in the multiscalar mode. The source consisted of ~10 mCi of ^{57}Co diffused into metallic rhodium, and a xenon gas proportional counter was used as the detector. The velocity transducer was calibrated in the conventional manner by employing the Mössbauer spectrum of metallic iron, and the linearity was found to be better than 0.5% for the velocity range. Mössbauer spectra were measured at 4.2 and 77 K by immersing the source and the sample holder directly into ligand helium and liquid nitrogen, respectively. The velocity scales and isomer shifts were measured relative to the Co(Rh) source, and the conversion to the α-iron standard at 295 K required the addition of 0.11 mm s^{-1}. All subsequent measurements were performed with the source, absorber, and detector in the same geometric arrangement. The accumulation of the Mössbauer spectrum of ^{57}Fe in natural abundance at 4.2 K required 10 days owing to the strong absorption of the 14.4-keV radiant energy by the high iodide content. Correction for the nonresonant background of the γ-rays was included in all the useful data, and the Mössbauer spectra were computer-fitted to Lorentzian line shapes with the aid of the Marburg Sperry 1100/62 facilities.[39] The resulting parameters were accurate to ±0.008 mm s^{-1}. Typically, a sample of FeI_3 (120 mg, combined from eight separate preparative batches) was loaded in the dark between a pair of Mylar films separated by a Teflon O-ring in an inert-atmosphere box. The sample holder was then placed in a light- and air-tight container that was flushed with thoroughly dry argon and immediately shipped by air express to Marburg.[24] Nonetheless, the partial decomposition of the highly labile ferric iodide during transit was unavoidable. Thus, inspection of the Mössbauer spectrum measured at 4 K indicated the presence of the components that are labeled as I, II, and III in Table III. The deconvolution of the experimental spectrum yielded the Mössbauer spectrum of the principal component I (45%) that consisted of six hyperfine lines with a ~ 3:2:1:1:2:3 intensity ratio, together with that of II (25%) with two resolved lines of equal intensity and that of III (30%) with a pair of partially resolved lines, each of which is represented by a smooth dashed curve in Figure 4A. The fit of the computed (composite) spectrum (shown as the smooth solid curve) in Figure 4B to the experimental data is unmistakable. Importantly, on the six-line hyperfine splittings of I disappeared at ~12 K, and the Mössbauer spectrum then consisted of a single broad absorption centered at ~0.1 mm s^{-1} with an additional weak absorption (~10%) at ~3.8 mm s^{-1}. This spectral change was confirmed by the fit in Figure 5 of the computer-simulated spectrum (shown by the solid smooth curve) to the experimental spectrum at 77 K. Indeed, the close correspondence in Table III between the set of optimized Mössbauer parameters evaluated at 4 and 77 K by computer simulation of II and III (dashed curves) supports the spectral assignment of the antiferromagnetic → paramagnetic transition[25] of phase I. Repetition of the Mössbauer experiment indicated the presence of the same three components I–III, albeit in slightly different relative amounts. However, when undue precaution was not exercised in the sample preparation, the amount of phase III increased (44%) largely at the expense of I (31%), and a new phase IV (~10%) was observed with a partially resolved sextet hyperfine splitting (δ ~ 0 mm s^{-1}) deduced by computer simulation of the Mössbauer spectrum. Indeed, the appearance of the

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(35) However such tetrahedral units with bridging iodide are expected to show significant quadrupole splittings (see ref 36, Chapter 3).

(36) Greenwood, N. N.; Gibb, T. C. *Mössbauer Spectroscopy*; Chapman and Hall: London, Chapters 6 and 7.

(37) The fluoro, chloro, and bromo consist of halo-bridged polymers with octahedral FeX_3 units.[38] Tetrahedral coordination of iron(III) in such polymeric units is unknown.

(38) (a) Ebert, F. *Z. Anorg. Chem.* **1931**, *196*, 395. (b) Ketelaar, J. A. A. *Nature* **1931**, *128*, 303. (c) Geiersberger, K. *Z. Anorg. Chem.* **1949**, *258*, 361. (d) Wooster, N. *Z. Kristallogr.* **1932**, *83*, 35. (e) Gregory, N. W. *J. Am. Chem. Soc.* **1951**, *73*, 472.

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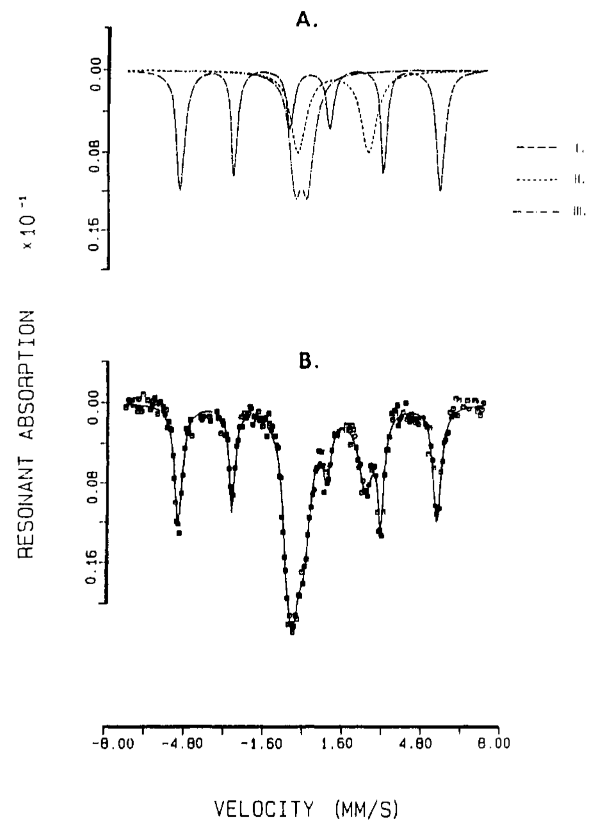

Figure 4. Mössbauer spectra from FeI_3 at 4.2 K: (A) deconvolutions based on phases I–III as indicated; (B) fit of the composite of the simulated spectra in (A) to the experimental data.

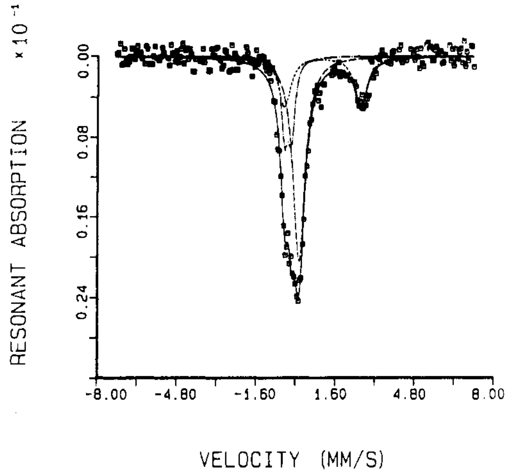

Figure 5. Mössbauer spectra of FeI_3 at 77 K: dashed curves, simulated spectra of II and III (as in Figure 4A) and of I (with H_{hf} = 0 kOe); solid curve, fit of the simulated (composite) spectrum to the experimental data.

phases II–IV in the sample of FeI_3 could be qualitatively traced to adventitious dioxygen in the following way. A newly prepared 50-mg sample of FeI_3 was carefully loaded into a Mössbauer spectrometer (Ranger Model MS-900 at Rice University) under red light in a dry dinitrogen atmosphere, and the vacuum chamber was quickly evacuated and cooled to 77 K (measurement at 4 K was not possible at this facility). The Mössbauer spectrum, after data collection for 2 days, appeared somewhat broadened, centered at δ 0 mm s^{-1} (compare Figure 5). Dry air (100 mL, STP) was then introduced directly into the vacuum chamber at 77 K, and the data acquisition was resumed. The Mössbauer spectrum after 4 h showed a new iron(II) phase (with $\delta \sim 1.2$ and $eQ \sim 2.8$ mm s^{-1}), which became dominant after 2 days. The precise measurement of the Mössbauer parameters for the new phase (compare II in Table III) was hampered by the presence of a relatively broad, residual absorption centered at ~0 mm s^{-1}. We thank S. A. Moy (Rice University) for assistance with the additional Mössbauer measurement at 77 K in the presence of dioxygen, as necessitated in Houston. These experiments thus confirm the deleterious effect of dioxygen on FeI_3 that lead to the observation of the two additional phases (II and III) in the Mössbauer spectrum, the parameters of which accord with those of high-spin iron(II) and low-spin iron(III), respectively.[36] Such adulterants could have easily resulted from the inadvertent exposure of the sample to either dioxygen, light, or moisture—toward which FeI_3 is extremely sensitive.[40]

Measurement of the Magnetic Susceptibility. The magnetic susceptibility of FeI_3 was measured on a Princeton Applied Research Model 155 vibrating-sample magnetometer under an argon atmosphere. The temperatures were measured with a calibrated GaAs diode and were accurate to ±1% of the absolute temperature. The applied magnetic fields of up to 2 T were measured with a Hall probe gaussmeter, and the magnetometer was calibrated with a sample of $Co[Hg(NCS)_4]$.[41] An 80-mg sample of FeI_3 (accumulated from six separate preparative runs) was pressed into a Kel-F sample holder (~3 mm diameter), and the magnetic susceptibility measured from 4.7 to 250 K in Marburg. The magnetic susceptibility of FeI_3 followed Curie–Weiss behavior with a negative Weiss temperature of $\Theta = -30$ K and a Curie constant of C = 2.46 emu K mol^{-1}. The somewhat limited magnitude of the magnetic moment (evaluated as $\mu_{eff} = (8C)^{1/2}$) of 4.4 μ_B for ferric iodide was probably due to the impurities. Indeed, if the contamination from phases II and III (vide supra) was considered to consist of high-spin iron(II) with S = 2 (25%) and paramagnetic iron(III) with $S = {}^1/_2$ (30%), respectively, the corrected magnetic moment of ~5.9 μ_B was consistent with that expected for high-spin FeI_3. It is noteworthy that a slight negative deviation of the magnetic susceptibility from Curie–Weiss behavior occurred at ~30 K, and it corresponded roughly to the temperature-dependent changes in the Mössbauer spectrum (vide supra).

Measurement of the Electronic Absorption Spectrum. Quantitative Conversion to Tetraiodoferrate(III). Iron pentacarbonyl (1.14 × 10^{-1} mmol) and diiodine (5.9 × 10^{-1} mmol) were dissolved in 200 mL of dried *n*-hexane under an argon atmosphere in the dark. A 5-mL aliquot was diluted with 45 mL of *n*-hexane, and 4.5 mL of this solution was introduced into a Schlenk type UV cell under an argon atmosphere. Upon the exposure of the sealed cuvette to diffuse room light for 1 h at 0 °C, a deep purple (black) solid appeared on the wall. The supernatant solution was removed with the aid of a Teflon cannula, and the dark deposit was washed under an argon atmosphere with small amounts of hexane and then dissolved in rigorously purified dichloromethane (3 mL). The electronic absorption spectrum (Hewlett-Packard Model 8450Å diode-array spectrometer) of the dark blue-violet solution is illustrated in Figure 1A (lower spectrum). The successive addition of iodide as the tetra-*n*-butylammonium salt dissolved in dichloromethane (4 mM) resulted in the appearance of a new absorption band at λ = 698 nm, which reached its maximum absorbance when a total of 1 equiv of iodide was added (relative to the $Fe(CO)_5$ initially charged). The absorption spectrum of FeI_4^- shown in Figure 1A (upper) was the same as that (Figure 1B) of an authentic sample of $n\text{-}Bu_4N^+FeI_4^-$ prepared according to the method of Pohl and Saak.[9]

Effect of Dioxygen on Iodoiron(III) Species in Solution. Extra dry dioxygen (Matheson, 99.6%) was further treated by slowly passing it through a column of a molecular sieve (Mallinckrodt 3A activated at 350 °C and 10^{-5} Torr for 3 h) that was cooled to −78 °C by immersion in a dry ice bath. *Decomposition of ferric iodide* (0.15 mM) in dichloromethane occurred immediately upon the introduction of dioxygen to afford a light pink solution together with fine light brown particles (not characterized). The spectral change corresponded to the disappearance of the characteristic absorption bands of ferric iodide in Figure 1 and the appearance of a new band of diiodine at λ = 504 nm.[19] Light scattering by the brown particles resulted in the base line shift. *Inhibition of ferric iodide formation* from a solution of 0.15 mM $Fe(CO)_5$ and 0.45 mM I_2 in the presence of dioxygen was noted as follows. Before the actinic irradiation, the absorption spectrum of the red solution simply consisted of the superposition of the $Fe(CO)_4I_2$ and I_2 spectra. Upon exposure to light, the absorption band of $Fe(CO)_4I_2$ with λ = 254 nm gradually diminished and the solution became increasingly turbid owing to the separation of fine particles (vide supra). The characteristic absorption spectrum of FeI_3 in Figure 1 was not observed throughout this experiment, the final light pink solution showing only the diiodine absorption. *Decomposition of tetraiodoferrate(III)* was significantly less sensitive to dioxygen than ferric iodide. Thus the intensity of the unique absorption band at λ = 698 nm (Figure 1B) decreased by only 30% over the course of 15 h. The slightly turbid solution showed a slight increase in absorbance at $\lambda \sim 500$ nm.

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(40) The disproportionation of FeI_3 could lead to iron(II) and triiodide, e.g., $2FeI_3 \rightarrow FeI^+I_3^- + FeI_3$. However the Mössbauer parameters for II in Table III are not consistent with FeI_2 (see Table II).

(41) Compare: Kohler, P.; Pebler, J.; Schmidt, K. *J. Solid State Chem.* **1979**, *28*, 279.

Acknowledgment. We are indebted to Dr. J. Pebler (Philipps Universität, Marburg, West Germany) for his invaluable assistance in the Mössbauer and magnetic susceptibility measurements and to S. A. Moy (Rice University, Houston) for additional Mössbauer measurements in the presence of dioxygen. We also thank the National Science Foundation and R. A. Welch Foundation for financial support and the Alexander von Humboldt Stiftung for a U.S. Senior Scientist award to J.K.K.

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EPR Study of Manganese(II) in Single Crystals of the Spin-Crossover Complex $[Fe(2\text{-}pic)_3]Cl_2\cdot C_2H_5OH$. Evidence for Domains in Transition

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The temperature-dependent spin-crossover transition ${}^5T \leftrightarrow {}^1A$ in the compounds $[Fe(2\text{-}pic)_3]X_2\cdot S$ (2-pic = 2-(aminomethyl)pyridine), with X = Cl or Br and S = C_2H_5OH or CH_3OH, was first reported by Renovitch and Baker.[1] The gradual nature of the transitions in these compounds sets them apart from most of the other Fe(II) systems studied to date.[2-4] Comparisons between the gradual spin crossover in these systems and the abrupt transitions observed in most other Fe(II) spin-crossover systems provide an excellent testing ground for proposed theoretical models.[5,6]

In an earlier paper, Rao et al.[7] used EPR of Mn(II)-doped powder samples of $[Fe(2\text{-}pic)_3]Cl_2\cdot C_2H_5OH$ to probe the interactions between molecules during the spin-crossover. Changes in the zero-field-splitting (ZFS) parameters D and E and the resonance line widths as a function of temperature were compared to those found in Mn(II)-doped samples of the Zn analogue. The ZFS parameters in both Zn and Fe systems increased gradually as the temperature was lowered with no unusual changes in the spin-crossover interval of the Fe compound. The resonance line widths in the Fe(II) samples did, however, increase dramatically in the temperature region of the spin-crossover transition. It is clear that some effect related to the crossover transition affects the line widths of the Mn(II) spectrum. Rao et al.[7] proposed that the broadening was due to the increasing spin lifetime of the high-spin Fe(II) as the temperature decreased, creating an effective dipolar broadening. Later ${}^1H$ NMR evidence[8] placed this explanation in doubt; the spin lifetimes were observed to stay short on the NMR time scale throughout the spin crossover.

Single-crystal EPR studies yield much more detailed information about the solid-state than power studies. Recent papers from this laboratory[9,10] reporting EPR studies of Mn(II) in single crystals of two other Fe(II) spin-crossover systems have shown the advantage of studying these transitions by using single-crystal EPR. With this in mind, we undertook to grow single crystals of $[Fe(2\text{-}pic)_3]Cl_2\cdot C_2H_5OH$ doped with small amounts of Mn(II).

Experimental Section

Sample Preparation. The ligand 2-(aminomethyl)pyridine was obtained from Aldrich Chemical Co. and used without further purification. Ethanol was dried by refluxing over Mg turnings, distilled under inert atmosphere, and degassed by repeated freeze–thaw cycles. All manipulations were carried out in a glovebag under nitrogen. $FeCl_2\cdot 2H_2O$ was prepared by using standard literature techniques.[11]

Powder samples of Mn(II)-doped $[Fe(2\text{-}pic)_3]Cl_2\cdot C_2H_5OH$ were made by following the techniques used by Rao et al.[7] using 2% (by mole) $MnCl_2\cdot 4H_2O$ and 98% $FeCl_2\cdot 2H_2O$. The fine yellowish powder gave an EPR spectrum identical with that reported earlier. Large single crystals were obtained by dissolving approximately 2 g of the doped powder into 200 mL of boiling ethanol. The resulting reddish brown solution was filtered while warm into a 350-mL three-neck flask containing ca. 50 mL of warm ethanol (55 °C). This solution was stoppered and allowed to cool slowly overnight. The solvent was evaporated by slowly blowing nitrogen over the surface of the liquid for a period of 3 weeks. Crystals were collected by pouring off the remaining ca. 30 mL of liquid and washing the crystals with small amounts of cold (0 °C) ethanol and hexane. The resulting yellowish brown crystals were dried under reduced pressure and then stored in a stoppered flask under nitrogen. This procedure commonly yielded a number of good sized (3 × 2 × 2 mm) parallelpiped-shaped crystals. The crystals tend to lose solvent over time, breaking into sheets of powder. Storage over strong drying agents, such as P_2O_5, or storage under an active vacuum will destroy the crystals in a short time.

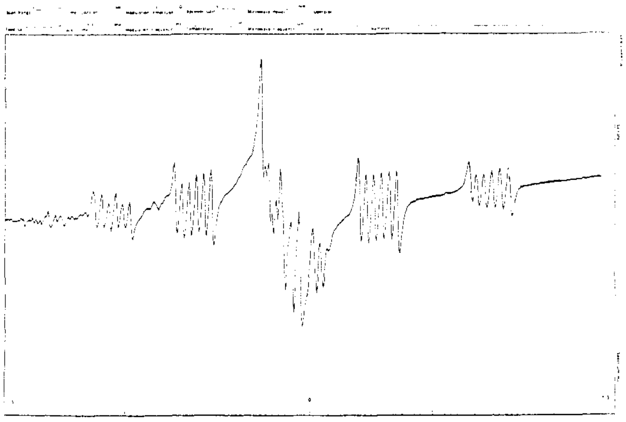

Figure 1. Room-temperature EPR spectrum of Mn(II) in single crystals of $[Fe(2\text{-}pic)_3]Cl_2\cdot C_2H_5OH$. Magnetic field is in the *ac* plane in the direction of maximum ZFS splitting.

EPR Spectra. The crystals were mounted on quartz capillaries with various cyanoacrylate adhesives[12] and sealed under vacuum in a 4.2-mm-o.d. quartz tube. EPR spectra were obtained on an X-band Varian E-12 spectrometer equipped with an E-231 rotating cavity and rotating magnet base. Variable-temperature spectra were obtained with a Varian nitrogen-flow temperature-control system. Spectra at 77 K were obtained by using a quartz finger Dewar. The magnetic field was calibrated by using an NMR magnetometer. The klystron frequency was calibrated with diphenylpicrylhydrazyl and the NMR magnetometer.

Results

Room-Temperature Spin Hamiltonian. X-ray structure determinations[6,13-16] for $[Fe(2\text{-}pic)_3]X_2\cdot C_2H_5OH$ show the system to be monoclinic $P2_1/c$ with four molecules in the unit cell. Symmetry requires that we detect two resonances in most orientations except when the magnetic field is in the *ac* plane. In Figure 1 is given the spectrum when the magnetic field is in the

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