2040 *Inorg. Chem.* **1985**, *24*, 2040–2046

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# Preparation, Structures, and Physical Properties of Two Products from the Iodination of (Phthalocyaninato)iron(II)

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*Received August 31, 1984*

(Phthalocyaninato)iron(II), Fe(pc), was oxidized in a solution of iodine in hot 1-chloronaphthalene. Two products were isolated: $[FeCl(pc)]_2I_2$, which is a new compound formed by reaction with the solvent, and the molecular conductor Fe(pc)I. $[FeCl(pc)]_2I_2$ crystallizes in space group $C_i^1$-$P\bar{1}$ of the triclinic system with 1 formula unit in a cell of dimensions $a$ = 12.270 (7) Å, $b$ = 13.202 (7) Å, $c$ = 8.335 (6) Å, $\alpha$ = 92.80 (3)°, $\beta$ = 97.17 (3)°, and $\gamma$ = 101.97 (2)° at 113 K. Full-matrix least-squares refinement of 388 variables gives a final value for $R$ (on $F_o^2$) of 0.066 for 6847 observations. The structure consists of two square-pyramidal FeCl(pc) units linked by $I_2$ via the axial chloro ligands. The four halogens form an essentially linear unit. The $^{57}$Fe Mössbauer spectrum is consistent with this structure. Fe(pc)I crystallizes in space group $D_{4h}^2$-$P4/mcc$ of the tetragonal system with 2 formula units in a cell of dimensions $a$ = 13.84 (2) Å and $c$ = 6.77 (1) Å at 97 K. Full-matrix least-squares refinement of 35 variables gives a final value of 0.177 for the $R$ index (on $F_o^2$) for 620 observations. The structure consists of chains of Fe(pc) molecules, stacked metal over metal. Adjacent Fe(pc) molecules in the unit cell are staggered by 40°. Disordered chains of $I_3^-$ lie in channels between the Fe(pc) stacks. The iodine is identified as $I_3^-$ by resonance Raman spectroscopy. The single-crystal conductivity of Fe(pc)I is 20 $\Omega^{-1}$ cm$^{-1}$ at 20 °C; the conductivity increases with decreasing temperature.

## Introduction

We are engaged in the synthesis of conductive molecular crystals by partial oxidation with iodine of metallophthalocyanines and metalloporphyrins.[1] However, $I_2$ oxidation of Fe(pc) in 1-chloronaphthalene solvent has produced an unexpected result: the isolation of *two* different products. We report the synthesis, characterization by electron microprobe and $^{57}$Fe Mössbauer spectroscopy, and the X-ray crystallographic structure of a new compound of composition $[FeCl(pc)]_2I_2$. The structure consists of two $Fe^{III}Cl(pc)$ units with the metal atoms slightly displaced from the phthalocyanine planes, which are face-to-face and bridged by an iodine molecule weakly coordinated to the axial chloro ligands. The four halogens form an essentially linear unit.

We also report the synthesis, physical characteristics, and structure of the molecular conductor Fe(pc)I, whose structure, consisting of metal-over-metal Fe(pc) stacks, is analogous to that of the highly conductive Ni(pc)I[2] and other related compounds.[1] The room-temperature conductivity of Fe(pc)I, of approximately 20 $\Omega^{-1}$ cm$^{-1}$, is much lower than that of Ni(pc)I.

## Experimental Section

Iron phthalocyanine (Fe(pc)) was purchased from Eastman Kodak Co. Elemental analysis[3] and optical spectra indicated that up to 30% of the material was metal-free phthalocyanine ($H_2$(pc)). In order to remove the $H_2$(pc), the coordinating properties of the four-coordinate iron center were employed.[4] In the presence of imidazole, Fe(pc) forms a six-coordinate compound, Fe(pc)$(Im)_2$, which is soluble in acetone, whereas $H_2$(pc) remains unligated. The Fe(pc) as received was first dissolved in molten imidazole, and the melt was cooled. The resulting green solid, consisting of Fe(pc)$(Im)_2$, excess imidazole, and $H_2$(pc), was extracted with acetone in a Soxhlet extractor, leaving behind the insoluble metal-free impurity. The Fe(pc)$(Im)_2$ solution was evaporated to dryness, and the remaining solid, consisting of Fe(pc)$(Im)_2$ and imidazole, was heated to 100 °C under vacuum to drive off the excess imidazole and the weakly bound imidazole ligands. Sublimation of the residual blue powder at 400 °C yielded red-violet needles of Fe(pc). Elemental analysis and optical spectra indicate that this material contains negligible amounts of $H_2$(pc). All starting material was purified in this manner. Anal. Calcd for $C_{32}H_{16}FeN_8$: C, 67.62; H, 2.84; N, 19.71. Found: C, 67.51; H, 2.98; N, 19.71.[3]

**Synthesis of Oxidized Materials.** The reaction of Fe(pc) with $I_2$ was carried out in a manner similar to that of Ni(pc) and $I_2$.[2] Fe(pc) and excess solid $I_2$ were reacted in 1-chloronaphthalene solvent in H-tubes that were heated to 110 °C on one side. This procedure was not routinely successful, but in a few cases black crystalline, oxidized material was obtained. Four such preparations yielded small amounts of crystals that were judged visually to warrant study, but the limited amounts posed experimental difficulties.

The crystals exhibit two distinct morphologies. Some are approximately parallelepipeds and are of good quality. The products of two of the preparations were of this type. The first, consisting of less than 1 mg of crystals, provided parallelepipeds large enough for a crystal structure determination, the largest crystals being on the order of 0.3 mm × 0.2 mm × 0.1 mm. The limited amount of material precluded most further experimentation on this batch. The other batch contained sufficient material for a C, H, and N analysis; it will be shown that the composition is $[FeCl(pc)]_2I_2$. Anal. Calcd for $C_{32}H_{16}ClFeIN_8$: C, 52.6; H, 2.2; N, 15.3. Found: C, 53.0; H, 2.5; N, 15.2.[3]

A third preparation was predominantly made up of needle-shaped crystals of poor quality. The needles will be shown, by electron microanalytical probe and X-ray studies, to have the composition Fe(pc)I. The fourth preparation was an approximately equal mixture of the two crystal types.

Chloro(phthalocyaninato)iron(III), FeCl(pc), was prepared by the method of Barrett et al.,[5] in order to provide a standard for analysis of the electron microprobe and Mössbauer data. Fe(pc) was heated over steam in a large excess of concentrated HCl in open air for 4 h. The blue-green solid, FeCl(pc), was filtered and washed with ethanol and diethyl ether. Myers et al.[6] report that this synthetic procedure can result in a nonhomogeneous product mixture containing both mono- and dichloro $Fe^{III}$(pc) products. However, elemental analysis of the FeCl(pc) we prepared indicates an Fe(pc):Cl ratio of very nearly 1. Anal. Calcd for $C_{32}H_{16}ClFeN_8$: C, 63.65; H, 2.67; N, 18.56; Cl, 5.87. Found: C, 63.13; H, 2.82; N, 18.39; Cl, 6.14.[3]

**X-ray Diffraction Study of $[FeCl(pc)]_2I_2$.** Single crystals of $[FeCl(pc)]_2I_2$ were grown as described above. On the basis of precession and Weissenberg X-ray photographs, the crystals were assigned to the triclinic system. Successful refinement of the structure supports the choice of space group $C_i^1$-$P\bar{1}$. The cell constants (Table I) were found by a least-squares refinement[7] of the setting angles of 20 reflections automatically centered on a FACS-I diffractometer with the use of graphite-monochromated Mo K$\alpha$ radiation.

Intensity data for Bragg scattering were collected at 113 (3) K by the $\theta$–$2\theta$ scan technique and were processed with a value of 0.03 for $p$.[7,8]

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(1) (a) Ibers, J. A.; Pace, L. J.; Martinsen, J.; Hoffman, B. M. *Struct. Bonding* (*Berlin*) **1982**, *50*, 1–55. (b) Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1983**, *16*, 15–21. (c) Hoffman, B. M.; Martinsen, J.; Pace, L. J.; Ibers J. A. In "Extended Linear Chain Compounds"; Miller, J. S.; Ed.; Plenum Press: New York, 1983; Vol. 3, pp 459–549.

(2) (a) Petersen, J. L.; Schramm, C. J.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288. (b) Schramm, C. J.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science* (*Washington, D.C.*) **1978**, *200*, 47–48. (c) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6713. (d) Martinsen, J.; Greene, R. L.; Palmer, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 677–678. (e) Martinsen, J.; Palmer, S. M.; Tanaka, J.; Greene, R. L.; Hoffman, B. M. *Phys. Rev. B*, **1984**, *30*, 6269–6276.

(3) Micro-Tech Laboratories, Inc., Skokie, IL.

(4) Sweigart, D.; Martinsen, J., private communication.

(5) Barrett, P. A.; Frye, D. A.; Linstead, R. P. *J. Chem. Soc.* **1938**, 1157–1163.

(6) Myers, J. F.; Rayner Canham, G. W.; Lever, A. P. B. *Inorg. Chem.* **1975**, *14*, 461–468.

(7) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197–204.

**Table I.** Crystal Data and Experimental Details for $[FeCl(pc)]_2I_2$ and Fe(pc)I

| compd | $[FeCl(pc)]_2I_2$ | Fe(pc)I |
|---|---|---|
| formula | $C_{64}H_{32}Cl_2Fe_2I_2N_{16}$ | $C_{32}H_{16}FeIN_8$ |
| fw | 1461.52 | 695.29 |
| $a$, Å | 12.270 (7) | 13.84 (2) |
| $b$, Å | 13.202 (7) | 13.84 (2) |
| $c$, Å | 8.335 (6) | 6.77 (1) |
| $\alpha$, deg | 92.80 (3) | 90.0 |
| $\beta$, deg | 97.17 (3) | 90.0 |
| $\gamma$, deg | 101.97 (2) | 90.0 |
| $V$, Å$^3$ | 1306 | 1320 |
| $Z$ | 1 | 2 |
| $d_{calcd}$, g/cm$^3$ | 1.857 (113 K)$^a$ | 1.779 (97 K)$^a$ |
| $d_{obsd}$,$^b$ g/cm$^3$ | 1.79 (5) (298 K) | |
| space gp | $C_i^1$-$P\bar{1}$ | $D_{4h}^2$-$P4/mcc$ |
| cryst shape | cryst bounded by faces $(0\bar{1}1)$, (201), (001), $\{0\bar{1}0\}$, {110}; max dimens 0.26 mm × 0.20 mm × 0.11 mm | needle of rectang cross section with dist between faces {001}, 0.826 mm; {100}, 0.076 mm; {010}, 0.060 mm |
| cryst vol, mm$^3$ | $2.55 \times 10^{-3}$ | $3.77 \times 10^{-3}$ |
| radiation | graphite-monochromated Mo K$\alpha$ ($\lambda$(Mo K$\alpha_1$) = 0.7093 Å) | |
| $\mu$, cm$^{-1}$ | 18.9 | 18.0 |
| transmissn factors | 0.719–0.887 | 0.930–0.943 |
| take-off angle, deg | 3.5 | 3.0 |
| receiving aperture | 4.5 mm high × 3.5 mm wide, 34 cm from cryst | 5.0 mm high × 5.5 mm wide, 34 cm from cryst |
| scan speed, deg in $2\theta$/min | 2 | 2 for first 515 reflcns; 1 thereafter |
| scan width, deg | 0.90 below $K_{\alpha_1}$ to 1.00 above $K_{\alpha_2}$ | 0.90 below $K_{\alpha_1}$ to 0.90 above $K_{\alpha_2}$ |
| bkgd counts | 20 s with rescan option$^c$ | 20 s with rescan option for first 515 reflections; 40 s with rescan option thereafter |
| data collcd | $\pm h, \pm k, l \geq 0$; $3.3° \leq 2\theta \leq 58.0°$ | $h \geq k \geq 0$, $l \geq 0$; $4 \leq 2\theta \leq 45.0°$ |
| no. of unique data after av | 6847 | 620 |
| no. of unique data with $F_o^2 \geq 3\sigma(F_o^2)$ | 4790 | 185 |
| no. of variables | 388 | 35 |
| $R$ on $F_o^2$ | 0.066 | 0.177 |
| $R_w$ on $F_o^2$ | 0.104 | 0.174 |
| $R$ on $F_o$ ($F_o^2 > 3\sigma(F_o^2)$) | 0.042 | 0.080 |
| $R_w$ on $F_o$ ($F_o^2 > 3\sigma(F_o^2)$) | 0.048 | 0.070 |
| error in observn of unit wt | $1.18e^2$ | $1.26e^2$ |

$^a$The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. $^b$Flotation in $ZnCl_2/H_2O$. $^c$The diffractometer was run under the disk-oriented Vanderbilt system: Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570.

Procedures for data collection and structure refinement were those standard in this laboratory.[8] No systematic change was detected in the intensities of six standard reflections that were measured every 100 reflections. A total of 6847 unique reflections was gathered, 4790 of which were found to have $F_o^2 > 3\sigma(F_o^2)$. Experimental details and crystal data are given in Table I.

With the exception of three carbon atoms, the positions of all non-hydrogen atoms were found by direct methods with the statistically weighted tangent formula of the MULTAN80 program package.[9] All 418 of the strongest reflections were used for phase determination, and idealized positions of atoms of a phthalocyanine fragment were input to the program. The remaining three carbon atoms were located from a difference electron density map.

Since Raman spectra of early batches of crystal mixtures indicated the presence of $I_3^-$, a solution to the structure was attempted that incorporated $I_3^-$, even though such a solution seemed to be incompatible with the Patterson map. The initial model obtained from direct methods had four atoms bridging between the two Fe atoms, the two closest to the Fe atoms having approximately half the electron density of the other two. A physical model that included $I_3^-$ was postulated. The $I_3^-$ ions were considered to be disordered, half coordinating to only one Fe atom of the dimer unit and half coordinating to the other Fe atom of the unit. One would expect to see effects of this disorder in large thermal parameters for the Fe and I atoms. Least-squares refinement of this model did not give abnormally large thermal parameters. Refinement of the occupancies of the two I positions resulted in values of 0.30 for the site closer to the Fe atom and 0.98 for the site farther from the Fe atom. Moreover, the Fe was 0.30 Å above the plane formed by the four coordinating N atoms with essentially no electron density in the plane of the ring, consistent with square-pyramidal coordination of the Fe atom.

The final model, which converged satisfactorily, accounts for the oxidation state of the Fe atoms and the normal thermal parameters of the I sites. It takes as the product of the iodination attempt two $Fe^{III}Cl(pc)$ units that are linked by $I_2$. Chlorine was chosen to represent the electron density in the site closest to the Fe atom because it has roughly one-third of the electrons of I and because it was present (as chloronaphthalene) in the reaction mixture. With the heavy atoms thus identified, the positions of the H atoms were found on a difference electron density map. They were then idealized (C–H = 0.95 Å), and their positions were not varied in the least-squares process for the remainder of the refinement. Each H atom was assigned a fixed isotropic thermal parameter equal to 1 Å$^2$ greater than that of the C atom to which it is bonded. After the final cycle of refinement on $F_o^2$ (including $F_o^2 < 0$) (388 variables, 6847 observations) the values of the indices $R$ and $R_w$ (on $F_o^2$) were 0.066 and 0.104. The final difference electron density map shows eight peaks near I and Cl that average 1.15 e/Å$^3$, but other than these, the map is essentially featureless. The final positional parameters are given in Table IIa. Table IIb presents anisotropic thermal parameters and hydrogen atom positions.[10] Root-mean-square amplitudes of vibration are given in Table III.[10] A listing of structure amplitudes is found in Table IV.[10] A minus sign preceding $|F_o|$ indicates a negative value for $F_o^2$.

**X-ray Diffraction Study of Fe(pc)I.** Weissenberg and precession X-ray photographs of needle-shaped crystals of Fe(pc)I were superimposable on those of Ni(pc)I, as are those of Ni(tbp)I, Co(pc)I, Cu(pc)I, and $H_2$(pc)I.[2c,11] Indeed, the pattern of diffuse scattering is the same for Ni(pc)I and Fe(pc)I. On the basis of these photographs the crystals of Fe(pc)I were assigned to the Laue group $4/mmm$. Systematic absences observed were $h0l$ and $hhl$ with $l$ odd, consistent with space groups

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[8] See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

[9] Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J.-P.; Woolfson, M. M. "MULTAN80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York (England) and Louvain (Belgium), 1980.

[10] See paragraph at end of paper regarding supplementary material.

[11] (a) tbp = tetrabenzoporphyrinato. (b) Martinsen, J.; Pace, L. J.; Phillips, T. E.; Hoffman, B. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 83–91. (c) Martinsen, J.; Stanton, J. L.; Hoffman, B. M.; Ibers, J. A., manuscript in preparation. (d) Martinsen, J.; Ogawa, M. Y.; Palmer, S. M.; Stanton, J. L.; Hoffman, B. M.; Ibers, J. A., unpublished results.

**Table IIa.** Positional Parameters for $[FeCl(pc)]_2I_2$

| atom | *x* | *y* | *z* |
|---|---|---|---|
| I | 0.060 110 (25) | 0.099 460 (22) | 0.530 986 (37) |
| Fe | 0.332 473 (43) | 0.340 358 (39) | 0.832 035 (67) |
| N(1) | 0.454 88 (25) | 0.295 55 (23) | 0.740 59 (39) |
| N(2) | 0.561 95 (26) | 0.458 69 (24) | 0.672 35 (39) |
| N(3) | 0.413 24 (25) | 0.482 96 (23) | 0.825 28 (39) |
| N(4) | 0.297 59 (26) | 0.575 40 (23) | 0.968 35 (38) |
| N(5) | 0.244 19 (26) | 0.389 26 (23) | 0.985 96 (39) |
| N(6) | 0.144 64 (25) | 0.225 96 (23) | 1.068 82 (40) |
| N(7) | 0.284 08 (26) | 0.200 84 (23) | 0.897 57 (38) |
| N(8) | 0.403 44 (27) | 0.109 12 (24) | 0.761 41 (41) |
| C(1) | 0.541 08 (30) | 0.357 36 (29) | 0.675 89 (46) |
| C(2) | 0.610 22 (31) | 0.293 50 (29) | 0.611 67 (46) |
| C(3) | 0.705 80 (32) | 0.318 28 (30) | 0.536 64 (49) |
| C(4) | 0.756 10 (33) | 0.237 81 (34) | 0.494 48 (53) |
| C(5) | 0.712 50 (35) | 0.135 39 (32) | 0.526 07 (53) |
| C(6) | 0.616 55 (34) | 0.110 40 (30) | 0.598 15 (50) |
| C(7) | 0.565 58 (31) | 0.191 01 (30) | 0.640 83 (48) |
| C(8) | 0.467 04 (32) | 0.193 97 (30) | 0.718 73 (47) |
| C(9) | 0.320 41 (31) | 0.114 39 (28) | 0.845 39 (49) |
| C(10) | 0.256 89 (31) | 0.022 84 (29) | 0.907 22 (49) |
| C(11) | 0.260 91 (35) | −0.080 47 (29) | 0.890 48 (51) |
| C(12) | 0.194 80 (35) | −0.148 46 (30) | 0.977 07 (54) |
| C(13) | 0.124 82 (34) | −0.113 57 (31) | 1.079 73 (55) |
| C(14) | 0.118 94 (32) | −0.010 71 (30) | 1.093 76 (51) |
| C(15) | 0.185 70 (32) | 0.057 38 (29) | 1.004 67 (49) |
| C(16) | 0.201 66 (31) | 0.168 74 (29) | 0.993 09 (48) |
| C(17) | 0.165 23 (30) | 0.327 70 (29) | 1.064 02 (46) |
| C(18) | 0.103 55 (30) | 0.392 52 (29) | 1.145 77 (46) |
| C(19) | 0.016 33 (34) | 0.367 87 (30) | 1.237 99 (50) |
| C(20) | −0.027 44 (32) | 0.450 27 (33) | 1.292 85 (50) |
| C(21) | 0.014 38 (33) | 0.551 74 (31) | 1.260 79 (49) |
| C(22) | 0.102 81 (32) | 0.575 88 (29) | 1.170 70 (47) |
| C(23) | 0.146 94 (30) | 0.494 43 (28) | 1.112 83 (45) |
| C(24) | 0.235 58 (30) | 0.490 95 (27) | 1.015 07 (46) |
| C(25) | 0.380 02 (30) | 0.570 56 (28) | 0.883 80 (46) |
| C(26) | 0.452 34 (31) | 0.662 30 (29) | 0.837 17 (48) |
| C(27) | 0.454 59 (32) | 0.766 71 (29) | 0.867 31 (50) |
| C(28) | 0.531 74 (34) | 0.836 68 (29) | 0.798 75 (52) |
| C(29) | 0.608 22 (33) | 0.802 84 (31) | 0.705 58 (50) |
| C(30) | 0.608 22 (32) | 0.698 43 (29) | 0.680 64 (48) |
| C(31) | 0.527 48 (31) | 0.628 50 (28) | 0.747 59 (44) |
| C(32) | 0.503 36 (30) | 0.516 53 (27) | 0.743 46 (45) |
| Cl | 0.202 708 (73) | 0.331 536 (71) | 0.601 33 (11) |

*P4/mcc* or *P4cc*. Successful refinement of the structure supports the choice of $D_{4h}^2$-*P4/mcc*. The cell constants (Table I) were found by a least-squares refinement[7] of the setting angles of 12 reflections automatically centered as described above.

Intensity data for Bragg scattering were collected at 97 (3) K by the $\theta$–$2\theta$ scan technique and were processed with a value of 0.03 for $p$.[7,8] No systematic change was observed in the intensities of six standard reflections that were measured every 100 reflections. The crystal was small and was of poor quality. Out of a total of 620 unique reflections that were measured, only 185 were found to have $F_o^2 > 3\sigma(F_o^2)$. Experimental details and crystal data are given in Table I.

The starting positional parameters for Fe(pc)I were those of Ni(pc)I; these were refined isotropically. Because of the small number of data with $F_o^2 > 3\sigma(F_o^2)$, only the I and Fe atoms were refined anisotropically. The positions of the H atoms were found on a difference electron density map. They were then idealized (C–H = 0.95 Å), and their positions were not varied throughout the remainder of the least-squares refinement process. Each H atom was given a fixed isotropic thermal parameter equal to 1 Å$^2$ greater than that of the C atom to which it is attached. Refinement of the occupancy of I resulted in 1.004 (5) I per Fe(pc) group. After the final refinement on $F_o^2$ (including $F_o^2 < 0$) (35 variables, 620 observations) the $R$ and $R_w$ indices (on $F_o^2$) were 0.177 and 0.174, respectively. Final positional parameters are listed in Table Va. (The atom-labeling scheme is the same as that of Ni(pc)I[2c].) Table Vb presents the anisotropic thermal parameters and the hydrogen atom positions.[10] Table VI[10] lists structure amplitudes.

**Electron Microanalytical Probe.** Electron microprobe analysis was obtained on a Cambridge Scientific Instruments, Ltd., Stereoscan S4 scanning electron microscope. Samples were mounted with double-stick tape.

**$^{57}$Fe Mössbauer Spectroscopy.** Spectra were recorded at room temperature on an Austin Science spectrometer operating in the constant-acceleration mode. The data were fitted by an iterative nonlinear least-squares procedure. All isomer shifts are quoted with respect to the center of sodium nitroprusside, which was used to calibrate the spectrometer.

**Table Va.** Positional Parameters for Fe(pc)I

| atom | *x* | *y* | *z* |
|---|---|---|---|
| I | $^1/_2$ | $^1/_2$ | $^1/_4$ |
| Fe | 0 | 0 | 0 |
| N(1) | 0.1235 (12) | 0.0598 (12) | 0 |
| N(2) | 0.0823 (13) | 0.2316 (14) | 0 |
| C(1) | 0.1476 (21) | 0.1579 (21) | 0 |
| C(2) | 0.2490 (15) | 0.1739 (14) | 0 |
| C(3) | 0.3063 (18) | 0.2525 (17) | 0 |
| C(4) | 0.4032 (18) | 0.2422 (20) | 0 |
| C(5) | 0.4431 (17) | 0.1523 (20) | 0 |
| C(6) | 0.3902 (20) | 0.0708 (18) | 0 |
| C(7) | 0.2930 (17) | 0.0829 (16) | 0 |
| C(8) | 0.2152 (14) | 0.0127 (23) | 0 |

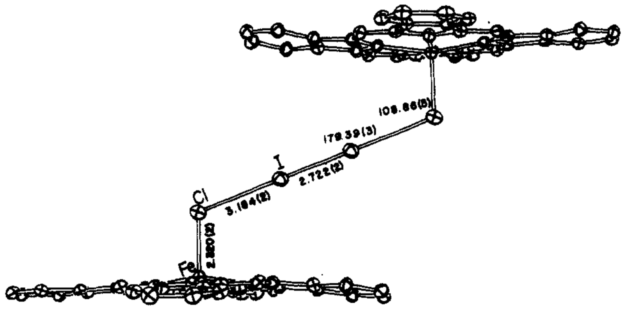

**Figure 1.** Perspective view of the centrosymmetric $[FeCl(pc)]_2I_2$ dimer.

**Resonance Raman Measurements.** Spectra were recorded on a 0.85-m Spex 1401 double monochromator spectrometer that employed 5145-Å Ar$^+$ excitation. Samples were studied in spinning 1-mm capillary tubes with a 180° back-scattering illumination geometry. A number of scans were made of each sample (the first at lowest possible laser power) to check for possible sample decomposition. Spectra were calibrated with the exciting line.

**Single-Crystal Electrical Conductivity Studies.** No conductivity data have been obtained on the exceedingly small crystals of $[FeCl(pc)]_2I_2$. Needle-shaped crystals of Fe(pc)I were mounted for four-probe ac conductivity measurements, as described elsewhere.[2c,d,12] Electrical contact to the crystals was made with a palladium paste.[13] The crystals were mounted on 8-$\mu$m graphite fibers (Alfa/Ventron). A four-probe ac technique, described previously,[12] was employed for measuring the sample resistance. Low temperatures were obtained with cold $N_2$ gas, and the temperature was monitored with a copper–constantan thermocouple.

The conductivity along the needle axis of the crystal ($\sigma_\parallel$) is defined in terms of a measured resistance ($R_\parallel$), crystal cross-sectional area ($A$) as estimated by the square of the maximum crystal width, and the distance between voltage probes ($L$): $\sigma_\parallel = L/(R_\parallel A)$. Dimensions of crystals mounted average 1.0 mm in length and 0.2 mm in width.

## Results

This study is one in a series aimed at comparing and contrasting the properties of iodine-oxidized metallo- and metal-free phthalocyanines and other related macrocycles.[1,2,11] From previous results,[2,11b–d] we expected the product of the oxidation of Fe(pc) by $I_2$ to consist of long, thin, bronze to green needles of oxidized Fe(pc), formulated as $[Fe(pc)]^{1/3+}(I_3^-)_{1/3}$, i.e., Fe(pc)I. However, the crystals obtained were either parallelepipeds or short, thick needles.

As discussed below, crystallographic investigation of the crystals prompted a series of experiments that demonstrate the existence of two different products: one is the proposed Fe(pc)I and the other is $[FeCl(pc)]_2I_2$, the chlorine being derived from the solvent.

**$[FeCl(pc)]_2I_2$. Description of the Structure.** The structure consists of two chloro(phthalocyaninato)iron(III) molecules bridged by an iodine molecule. Bond distances and angles are

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(13) Palladium paste is prepared by grinding palladium powder (0.25–0.55 $\mu$m, Alfa/Ventron) into a base of Pactra AeroGloss clear dope.

**Table VII.** Observed Distances and Angles in $[FeCl(pc)]_2I_2$

| Distances, Å | | | |
|---|---|---|---|
| I–I′ | 2.722 (1) | C(5)–C(6) | 1.375 (6) |
| I–Cl | 3.184 (2) | C(6)–C(7) | 1.395 (5) |
| Cl–Fe | 2.320 (2) | C(7)–C(8) | 1.448 (5) |
| Fe–N(1) | 1.949 (3) | C(9)–C(10) | 1.451 (5) |
| Fe–N(3) | 1.944 (3) | C(10)–C(11) | 1.376 (5) |
| Fe–N(5) | 1.947 (3) | C(10)–C(15) | 1.392 (5) |
| Fe–N(7) | 1.941 (3) | C(11)–C(12) | 1.376 (6) |
| N(1)–C(1) | 1.379 (5) | C(12)–C(13) | 1.411 (6) |
| N(1)–C(8) | 1.386 (5) | C(13)–C(14) | 1.375 (6) |
| N(2)–C(1) | 1.311 (5) | C(14)–C(15) | 1.394 (5) |
| N(2)–C(32) | 1.320 (5) | C(15)–C(16) | 1.452 (5) |
| N(3)–C(25) | 1.390 (5) | C(17)–C(18) | 1.452 (5) |
| N(3)–C(32) | 1.378 (5) | C(18)–C(19) | 1.388 (5) |
| N(4)–C(24) | 1.318 (5) | C(18)–C(23) | 1.394 (5) |
| N(4)–C(25) | 1.313 (5) | C(19)–C(20) | 1.391 (6) |
| N(5)–C(17) | 1.380 (5) | C(20)–C(21) | 1.383 (6) |
| N(5)–C(24) | 1.380 (5) | C(21)–C(22) | 1.388 (6) |
| N(6)–C(16) | 1.320 (5) | C(22)–C(23) | 1.392 (5) |
| N(6)–C(17) | 1.318 (5) | C(23)–C(24) | 1.445 (5) |
| N(7)–C(9) | 1.379 (5) | C(25)–C(26) | 1.446 (5) |
| N(7)–C(16) | 1.376 (5) | C(26)–C(27) | 1.383 (5) |
| N(8)–C(8) | 1.318 (5) | C(26)–C(31) | 1.384 (5) |
| N(8)–C(9) | 1.317 (5) | C(27)–C(28) | 1.378 (5) |
| C(1)–C(2) | 1.443 (5) | C(28)–C(29) | 1.416 (6) |
| C(2)–C(3) | 1.385 (5) | C(29)–C(30) | 1.384 (6) |
| C(2)–C(7) | 1.396 (5) | C(30)–C(31) | 1.398 (5) |
| C(3)–C(4) | 1.386 (6) | C(31)–C(32) | 1.444 (5) |
| C(4)–C(5) | 1.398 (6) | | |
| Angles, deg | | | |
| I′–I–Cl | 179.39 (2) | N(8)–C(9)–C(10) | 121.54 (34) |
| I–Cl–Fe | 108.86 (6) | C(9)–C(10)–C(11) | 132.15 (36) |
| Cl–Fe–N(1) | 101.05 (11) | C(9)–C(10)–C(15) | 106.54 (33) |
| Cl–Fe–N(3) | 98.16 (10) | C(11)–C(10)–C(15) | 121.24 (36) |
| Cl–Fe–N(5) | 97.22 (11) | C(10)–C(11)–C(12) | 117.94 (38) |
| Cl–Fe–N(7) | 99.16 (10) | C(11)–C(12)–C(13) | 121.13 (37) |
| N(1)–Fe–N(3) | 88.09 (13) | C(12)–C(13)–C(14) | 120.94 (37) |
| N(1)–Fe–N(5) | 161.72 (14) | C(13)–C(14)–C(15) | 117.44 (37) |
| N(1)–Fe–N(7) | 88.93 (13) | C(10)–C(15)–C(14) | 121.26 (35) |
| N(3)–Fe–N(5) | 88.82 (13) | C(10)–C(15)–C(16) | 106.75 (33) |
| N(3)–Fe–N(7) | 162.68 (14) | C(14)–C(15)–C(16) | 131.96 (37) |
| N(5)–Fe–N(7) | 88.67 (13) | N(6)–C(16)–N(7) | 128.09 (34) |
| Fe–N(1)–C(1) | 126.77 (25) | N(6)–C(16)–C(15) | 122.51 (34) |
| Fe–N(1)–C(8) | 125.96 (25) | N(7)–C(16)–C(15) | 109.39 (33) |
| C(1)–N(1)–C(8) | 107.14 (30) | N(5)–C(17)–N(6) | 128.00 (34) |
| C(1)–N(2)–C(32) | 122.11 (32) | N(5)–C(17)–C(18) | 109.50 (31) |
| Fe–N(3)–C(25) | 125.33 (25) | N(6)–C(17)–C(18) | 122.51 (34) |
| Fe–N(3)–C(32) | 126.72 (25) | C(17)–C(18)–C(19) | 131.51 (36) |
| C(25)–N(3)–C(32) | 107.39 (30) | C(17)–C(18)–C(23) | 106.45 (32) |
| C(24)–N(4)–C(25) | 121.41 (32) | C(19)–C(18)–C(23) | 122.03 (35) |
| Fe–N(5)–C(17) | 126.00 (25) | C(18)–C(19)–C(20) | 116.32 (35) |
| Fe–N(5)–C(24) | 125.64 (25) | C(19)–C(20)–C(21) | 122.36 (35) |
| C(17)–N(5)–C(24) | 107.54 (30) | C(20)–C(21)–C(22) | 120.92 (36) |
| C(16)–N(6)–C(17) | 121.34 (32) | C(21)–C(22)–C(23) | 117.68 (35) |
| Fe–N(7)–C(9) | 125.60 (25) | C(18)–C(23)–C(22) | 120.68 (35) |
| Fe–N(7)–C(16) | 126.49 (26) | C(18)–C(23)–C(24) | 106.94 (32) |
| C(9)–N(7)–C(16) | 107.72 (30) | C(22)–C(23)–C(24) | 132.38 (35) |
| C(8)–N(8)–C(9) | 120.88 (33) | N(4)–C(24)–N(5) | 127.92 (33) |
| N(1)–C(1)–N(2) | 127.42 (34) | N(4)–C(24)–C(23) | 122.49 (33) |
| N(1)–C(1)–C(2) | 109.55 (32) | N(5)–C(24)–C(23) | 109.56 (31) |
| N(2)–C(1)–C(2) | 123.02 (33) | N(3)–C(25)–N(4) | 128.42 (33) |
| C(1)–C(2)–C(3) | 131.67 (36) | N(3)–C(25)–C(26) | 109.12 (32) |
| C(1)–C(2)–C(7) | 107.35 (33) | N(4)–C(25)–C(26) | 122.46 (34) |
| C(3)–C(2)–C(7) | 120.96 (35) | C(25)–C(26)–C(27) | 131.32 (37) |
| C(2)–C(3)–C(4) | 117.46 (36) | C(25)–C(26)–C(31) | 106.88 (33) |
| C(3)–C(4)–C(5) | 121.61 (36) | C(27)–C(26)–C(31) | 121.80 (35) |
| C(4)–C(5)–C(6) | 121.00 (37) | C(26)–C(27)–C(28) | 117.47 (37) |
| C(5)–C(6)–C(7) | 117.64 (37) | C(27)–C(28)–C(29) | 121.11 (36) |
| C(2)–C(7)–C(6) | 121.31 (36) | C(28)–C(29)–C(30) | 121.12 (35) |
| C(2)–C(7)–C(8) | 105.96 (33) | C(29)–C(30)–C(31) | 116.92 (36) |
| C(6)–C(7)–C(8) | 132.73 (37) | C(26)–C(31)–C(30) | 121.50 (35) |
| N(1)–C(8)–N(8) | 128.15 (35) | C(26)–C(31)–C(32) | 107.15 (32) |
| N(1)–C(8)–C(7) | 109.96 (33) | C(30)–C(31)–C(32) | 131.35 (35) |
| N(8)–C(8)–C(7) | 121.88 (35) | N(2)–C(32)–N(3) | 127.23 (33) |
| N(7)–C(9)–N(8) | 128.85 (34) | N(2)–C(32)–C(31) | 123.34 (33) |
| N(7)–C(9)–N(10) | 109.48 (32) | N(3)–C(32)–C(3) | 109.42 (32) |

[a] I′ denotes the atom related to I by a center of symmetry, as shown in Figure 1.

**Table VIII.** Structural Data of Some Five-Coordinate Iron Porphyrin Halides

| compd | X | av dist, Å |  | $Fe-N_4$ plane, Å |
|---|---|---|---|---|
|  |  | Fe–X | Fe–N |  |
| $[FeCl(pc)]_2I_2$[a] | Cl | 2.320 (2) | 1.945 (3) | 0.30 |
| FeF(tpp)[b,c] | F | 1.792 (3) | 2.072 (1) | 0.47 |
| FeCl(tpp)[d] | Cl | 2.193 (3) | 2.060 (3) | 0.39 |
| FeBr(tpp)[e] | Br | 2.348 (2) | 2.06 (9) | 0.49 |
| FeI(tpp)[f] | I | 2.554 (3) | 2.066 (11) | 0.53 |
| FeCl(*N*-Metpp)[g,h] | Cl | 2.244 (1) | 2.161 (2) | 0.66 |

[a] This work. [b] tpp = 5,10,15,20-tetraphenylporphyrinato. [c] Reference 16. [d] Reference 17. [e] Reference 18. [f] Reference 19. [g] *N*-Metpp = *N*-methyl-5,10,15,20-tetraphenylporphyrinato. [h] Reference 20.

**Table IX.** Inter-Halogen Distances in Compounds with $(X-I-I-X)^{2-}$ Units

| compd | X | dist, Å |  |
|---|---|---|---|
|  |  | X–I | I–I |
| $I_2(g)$[a] |  |  | 2.662 |
| $I_2$(s, −163 °C)[b] |  |  | 2.715 (6) |
| $[Cu(C_9H_{15}N_5)I_2]\cdot{}^1/_2I_2$[c] | I | 3.353 (4) | 2.806 (4) |
| $MeAs(Me_2NCS_2)I_2$[d] | I | 3.357 (1) | 2.791 (1) |
|  |  | 3.436 (1) | 2.802 (1) |
| $Pt(phen)I_6$[e] | I | 3.481 (3) | 2.750 (3) |
|  |  | 3.452 (3) |  |
| $Pt(phen)I_5$[e] | I | 3.457 (3) | 2.739 (3) |
|  |  | 3.289 (3) |  |
| $Cu(NH_3)_4I_4$[f] | I | 3.342 (1) | 2.802 (1) |
| $Pd(C_2H_2(PC_6H_5)_4)I_2\cdot I_2$[g] | I | 3.527 (1) | 2.745 (1) |
|  |  | 3.483 (1) |  |
| $[Fe[S_2CN(CH_2)_4]_2I]\cdot{}^1/_2I_2$[h] | I | 3.516 (3) | 2.779 (3) |
| $Ru(Me_2NCS_2)_3I_3$[i] | I | 3.379 (3) | 2.834 (5) |
| $\{Ir(C_5Me_5)\}_2I_6$[j] | I | 3.241 (2) | 2.787 (2) |
|  |  | 3.557 (2) |  |
| $Me_2TeI_4$[k] | I | 3.404 (2) | 2.763 (2) |
|  |  | 3.456 (2) | 2.748 (2) |
| $Cd(NH_3)_4I_2\cdot I_2$[l] | I | 3.386 (2) | 2.793 (2) |
| $[FeCl(pc)]_2I_2$[m] | Cl | 3.184 (2) | 2.722 (1) |
| $SbCl_3\cdot I_2\cdot S_2C_4H_8$[n] | Cl, S[o] | 3.157 (2)[p] | 2.818 (1) |
|  |  | 2.717 (1)[q] |  |

[a] Reference 14. [b] Reference 15. [c] Reference 21. [d] Reference 22. [e] Reference 23. [f] Reference 24. [g] Reference 25. [h] Reference 26. [i] Reference 27. [j] Reference 28. [k] Reference 29. [l] Reference 30. [m] This work. [n] Reference 31. [o] In this structure, the $I_2$ is weakly coordinated to a covalently bound Cl of $SbCl_3$ and to a sulfur atom of dithiane. [p] Cl–I distance. [q] S–I distance.

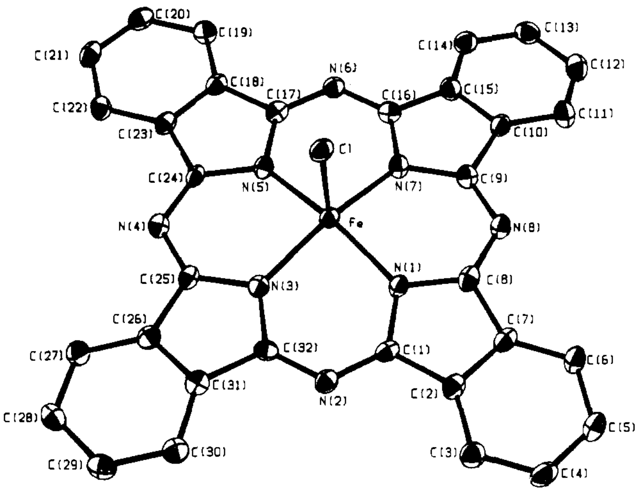

**Figure 2.** View of the FeCl(pc) unit of $[FeCl(pc)]_2I_2$ showing labeling scheme. Hydrogen atoms have been omitted.

listed in Table VII. The $I_2$ molecule connects the two FeCl(pc) groups via their axial chloro ligands, as shown in Figure 1. The phthalocyanine rings are related by a center of symmetry at the center of the I–I bond. We formulate the compound as neutral $I_2$ coordinated to FeCl(pc) since the I–I distance is nearly as short as it is in $I_2$.[14,15] The Fe atom is five-coordinate, having distorted square-pyramidal geometry. It lies 0.30 Å above the plane formed by the four coordinating N atoms.

There are no structures previously reported for five-coordinate (phthalocyaninato)iron compounds. Myers et al.[6] report that FeCl(pc) is unstable in solution. Some structural parameters for five-coordinate iron porphyrin halides[16-20] are listed in Table VIII for comparison. The main difference between the phthalocyanine and the porphyrin rings is that the methine bridges of porphyrins are more flexible than the azomethine bridges of phthalocyanines. Thus, the central hole formed by the four pyrrole N atoms is larger in porphyrins than in phthalocyanines, which accounts for the shorter Fe–N bond lengths in the latter. For $[FeCl(pc)]_2I_2$ the Fe–Cl bond length compares well with the other Fe–Cl bond lengths listed. But in this compound the Fe atom is closer to the $N_4$ plane, perhaps because of the shorter Fe–N bonds and the greater overall planarity of the phthalocyanine ring.

Relatively few structures have been reported for compounds having molecular iodine coordinated between two halide ions. In nearly all of these however, the $I_2$ is coordinated between two iodide ions.[21-31] Structural data are given for comparison in Table IX. If account is taken of the 0.21-Å difference in ionic radius between $Cl^-$ and $I^-$,[32] the $Cl^-$–I distance compares well with the $I^-$–I distances listed in Table IX. The $I_4^{2-}$ ion has been observed as an isolated anion as well as in polyiodide chains and networks.[33] But inclusion of chloride into these structures has not been reported. Keil[31] has reported the structure of $SbCl_3\cdot I_2\cdot S_2C_4H_8$, in which the iodine molecule is weakly coordinated to a covalently bound chlorine atom of $SbCl_3$ and a sulfur atom of dithiane. The Cl–I distance of 3.157 (2) Å compares favorably with that of 3.184 (2) Å in $[FeCl(pc)]_2I_2$.

Although the phthalocyanine ring, shown in Figure 2, possesses no imposed crystallographic symmetry, distances and angles for chemically equivalent bonds do not differ significantly and compare well with bond distances and angles of other phthalocyanine structures.[34] The benzo groups of the pc ring in $[FeCl(pc)]_2I_2$

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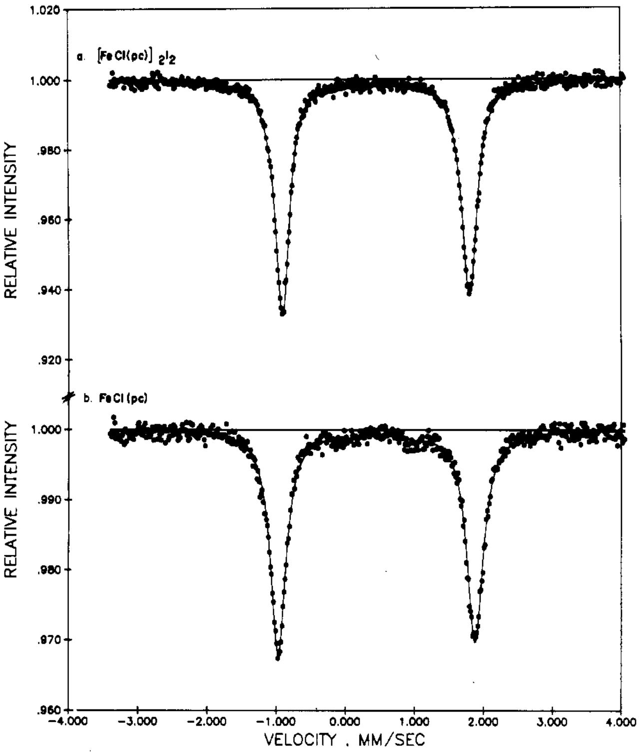

**Figure 4.** $^{57}$Fe Mössbauer spectra of (a) $[FeCl(pc)]_2I_2$ and (b) FeCl(pc). The solid line represents the optimized fit to the data points shown. Velocity is in mm/s. IS and QS values are given in Table XI.

**Table X.** Mössbauer Parameters of (Phthalocyaninato)iron(III) Species

| matl | QS, mm/s | IS,[a] mm/s |
|---|---|---|
| FeCl(pc)[b] | 2.711 (5) | 0.448 (5) |
| FeCl(pc)[c] | 2.748 (10) | 0.457 (10) |
| FeCl(pc)[d] | 2.75 | 0.46 |
| $[FeCl(pc)]_2I_2$[e] | 2.847 (5) | 0.453 (5) |
|  | 1.02 (3)[f] | 0.45 (3)[f] |
| FeBr(pc)[d] | 3.16 | 0.37 |
| $Fe(O_3SC_6H_9CH_3)(pc)$[d] | 3.95 | 0.49 |
| $FeI_2(pc)$[d] | 3.30 | 0.44 |
| $FeCl_2(pc)$[g] | 2.15 | 0.35 |

[a] Isomer shifts are reported with respect to the center of sodium nitroprusside. [b] This work; single phase. [c] Reference 35. [d] Reference 36, $O_3SC_6H_9CH_3^-$ = *p*-toluenesulfonate. [e] This work. [f] 3.5% (Fe basis) impurity. [g] Reference 37.

**Table XI.** Bond Distances and Angles for Fe(pc)I

| Distances, Å |  |  |  |
|---|---|---|---|
| Fe–N(1) | 1.90 (2) | C(2)–C(7) | 1.40 (3) |
| N(1)–C(1) | 1.40 (3) | C(3)–C(4) | 1.35 (3) |
| N(1)–C(8) | 1.43 (3) | C(4)–C(5) | 1.36 (3) |
| N(2)–C(1) | 1.36 (4) | C(5)–C(6) | 1.34 (3) |
| N(2)–C(8) | 1.33 (4) | C(6)–C(7) | 1.36 (3) |
| C(1)–C(2) | 1.42 (3) | C(7)–C(8) | 1.45 (3) |
| C(2)–C(3) | 1.34 (3) |  |  |

| Angles, deg |  |  |  |
|---|---|---|---|
| Fe–N(1)–C(1) | 130 (2) | C(2)–C(3)–C(4) | 120 (2) |
| Fe–N(1)–C(8) | 127 (2) | C(3)–C(4)–C(5) | 120 (3) |
| C(1)–N(1)–C(8) | 103 (2) | C(4)–C(5)–C(6) | 123 (3) |
| C(1)–N(2)–C(8) | 122 (2) | C(5)–C(6)–C(7) | 116 (3) |
| N(1)–C(1)–N(2) | 125 (2) | C(2)–C(7)–C(6) | 123 (2) |
| N(1)–C(1)–C(2) | 113 (3) | C(2)–C(7)–C(8) | 106 (2) |
| N(2)–C(1)–C(2) | 122 (2) | C(6)–C(7)–C(8) | 131 (2) |
| C(1)–C(2)–C(3) | 135 (2) | N(1)–C(8)–N(2) | 127 (2) |
| C(1)–C(2)–C(7) | 107 (2) | N(1)–C(8)–C(7) | 111 (2) |
| C(3)–C(2)–C(7) | 118 (2) | N(2)–C(8)–C(7) | 122 (2) |

appear to be slightly bent away from the Fe atom. The largest deviation from a least-squares plane of the phthalocyaine ring is in the benzo group closest to the coordinated $I_2$, with atom C(13) lying 0.28 Å below the plane.

Within the unit cell, parts of two phthalocyaine rings of two different bridged units are sandwiched between two phthalocyanine rings of another bridged unit, as shown in Figure 3.[10] The closest nonbonded contact between rings is 3.158 (6) Å between atoms C(29) and C(16) of two rings that lie face-to-face.

**Electron Microprobe Analysis.** Because the presence of Cl was postulated in the X-ray structure determination just described, analysis by electron microprobe was performed on crystals from each preparation in order to confirm the presence of chlorine and to quantitate the amount present. FeCl(pc) and the material that was analyzed to have the composition $[FeCl(pc)]_2I_2$ provided calibration standards. Crystals from the preparation that provided the parallelepipeds used in the X-ray structure determination show an Fe:Cl:I ratio of approximately 1:1:1, in agreement with the crystal structure results.

**Iron-57 Mössbauer Spectroscopy.** Figure 4a presents the room-temperature Mössbauer spectrum of a sample of $[FeCl(pc)]_2I_2$ that had been characterized by elemental and electron microprobe analyses. The spectrum consists of a quadrupole doublet with values of 2.85 mm/s for the quadrupole splitting (QS) and 0.45 mm/s for the isomer shift (IS) (Table X). The spectrum also contains a doublet from a minor impurity. The spectroscopic parameters for this impurity, which represents approximately 3.5% of the iron present, are also listed in Table X. The Mössbauer parameters of $[FeCl(pc)]_2I_2$ can be interpreted by comparison with literature values for $Fe^{III}$ phthalocyanines with various axial ligands[35-37] (Table X) and those we have obtained for FeCl(pc) (Figure 4b). These reference data and theory[37,38] indicate the Fe compounds having an IS ~ 0.45 mm/s correspond to $Fe^{III}$, with the value of QS being dependent upon the donor power of the ligand.[39] Thus, the IS value of 0.45 mm/s and the QS value of 2.85 mm/s measured for $[FeCl(pc)]_2I_2$ suggest an $Fe^{III}$(pc) species with an axial chloro ligand (Table X). This is consistent with the structural description of a pentacoordinate iron species. From the systematics of Table X, one would expect Fe(pc)I to have a QS larger than 3.3 mm/s.

The minor impurity doublet of $[FeCl(pc)]_2I_2$ has parameters (Table X) that are difficult to interpret. The IS suggests an $Fe^{III}$ ion, but there is no known or expected $Fe^{III}$(pc) compound with such a small value of QS.

**Resonance Raman Spectroscopy.** The Raman spectra of $[FeCl(pc)]_2I_2$ exhibit no scattering in the frequency region 50–650 cm$^{-1}$. Apparently the weak coordination of $I_2$ to the axial Cl atoms suppresses the expected vibrational band of $I_2$ at $\nu \sim 200$ cm$^{-1}$.

**Fe(pc)I. Electron Microprobe Analysis.** Results from electron microprobe analysis of the other batches of crystals varied from batch to batch and from particle to particle within a batch. In fact, some needle-shaped crystallites show Fe:I ratios of 1:1 with no detectable Cl and large, thick, needle-like crystals sometimes show variable composition across a single crystal. The observation of needle-shaped particles without Cl and with an Fe:I ratio of

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(39) (a) The Mössbauer spectrum of FeCl(pc) (Figure 4b) consists of a simple quadrupole doublet with no additional peaks. The QS value of 2.71 mm/s and IS value of 0.45 mm/s are in good agreement with those previously reported for this compound,[35-37] and the spectrum shows that there is at most 2% $FeCl_2$(pc).[37] This result, along with the observation of line widths almost equal to the minimum attainable on the spectrometer (0.25 mm/s), strongly indicates that the material is indeed a homogeneous, single phase. (b) Some controversy has existed about the Mössbauer spectrum of FeCl(pc). However, in an earlier work,[40] the valence of Fe in FeCl(pc) prepared in this way was shown to be 3+ by quantitative oxidative titration. Furthermore, theoretical justification for the interpretation of the spectrum in terms of an $Fe^{III}$ species is derived from an MO calculation for planar Fe(pc).[37]

(40) Elvidge, J. A. *J. Chem. Soc.* **1961**, 869–871.

approximately 1:1, in conjunction with other experimental evidence, led us to believe that Fe(pc)I also was being formed. This was confirmed by a crystal structure determination.

**Description of the Structure.** As expected, the structure of Fe(pc)I is similar to that of Ni(pc)I[2c] and its structural analogues, Ni(tbp)I, Co(pc)I, Cu(pc)I, and $H_2$(pc)I.[11] The crystal packing of Fe(pc)I is the same as that in Ni(pc)I, consisting of metallophthalocyanine stacks that are segregated from linear chains of iodine, both of which run parallel to the *z* axis. The iodine chains lie in channels formed by the benzo groups of neighboring chains of Fe(pc) molecules. Each Fe(pc) molecule is centered on a site of $4/m$ symmetry and so is constrained to be planar and perpendicular to the stacking axis. The two Fe(pc) molecules in the unit cell are staggered by 40° with respect to one another. Bond distances and angles for Fe(pc)I are given in Table XI. The most striking difference between the structure of Fe(pc)I and the other isostructural compounds is the relatively larger interplanar spacing. A comparison between the isostructural series of compounds will be discussed later.[11c]

Since the diffuse scattering observed in the photographs of Fe(pc)I matches that observed for Ni(pc)I and since the same amount of iodine is present in both structures, we believe that the model for the disorder of the $I_3^-$ chains in Ni(pc)I[2c] is applicable to Fe(pc)I as well.

**Resonance Raman Spectroscopy.** Resonance Raman spectra of preparations that were at least 50% needles show characteristic $I_3^-$ patterns[41] in the region 50–650 $cm^{-1}$. The spectra exhibit the intense totally symmetric stretching fundamental of $I_3^-$ at 107 $cm^{-1}$, along with the characteristic overtones at 211 and 315 $cm^{-1}$. The presence of $I_3^-$ supports the presumption that Fe(pc)I should be formulated $[Fe(pc)]^{1/3+}(I_3^-)_{1/3}$, as is true for Ni(pc)I. This experiment does not lend itself to a quantitative determination of Fe(pc)I in the product mixture.

**Conductivity Measurements.** The only crystals large enough to be mounted for conductivity measurements are of visibly poor quality, and thus well-defined, reliable conductivity behavior is difficult to obtain. However, the room-temperature conductivity of irregularly shaped needles is approximately 20 $\Omega^{-1}$ $cm^{-1}$, and variable-temperature studies on different crystals show a slight rise in conductivity below room temperature followed by a decrease in conductivity with temperature below 200 K. The room-temperature conductivity level is low compared with that of Ni(pc)I; this may in part reflect the larger interplanar spacing (3.38 Å for Fe(pc)I compared with 3.20 Å for Ni(pc)I).

After the conductivity experiment was performed, the Fe(pc)I crystals were removed from their mounts and soaked in octyl acetate and acetone to remove the palladium paste. These crystals were then mounted for microprobe analysis, which confirmed the Fe:I ratio of 1:1 and showed no evidence of chlorine.

## Conclusions

We have observed that the oxidation of Fe(pc) by $I_2$ in 1-chloronaphthalene results in the formation of two different products. The first, $[FeCl(pc)]_2I_2$, arises from the reaction between Fe(pc), $I_2$, and the solvent. Earlier Taube[37] reported that Fe(pc) reacts in hot chloronaphthalene to form FeCl(pc). However, the compound $[FeCl(pc)]_2I_2$ is new. There are no structural analogues known that contain either the $Cl^-$–I–I–$Cl^-$ unit or the five-coordinate Fe(pc)Cl subunit. From an analysis of Mössbauer spectra and the interatomic distances, the structure is interpreted as two FeCl(pc) units bridged by a neutral $I_2$ molecule via the axial chloro ligands. As shown in Table IX, $I_2$ forms bridges between two halide ligands in a variety of compounds, but $[FeCl(pc)]_2I_2$ represents the first $I_2$ bridge between two Cl ligands.

The striking difference in structure between the two products is evident even in their distinct crystal morphologies. The second product, Fe(pc)I, is a one-dimensional molecular conductor whose structure is like that of the other M(pc)I and related compounds.[1,2] The electrical conductivity along the needle axis is moderately high but is an order of magnitude lower than that of Ni(pc)I. The absence of an EPR signal has prevented a determination of the site of oxidation, namely metal or ligand. It is clear that Fe(pc)I is analogous to Ni(pc)I because of the identical structures and similar metallic conductivity.

**Acknowledgment.** We thank Dr. Alexander Shapiro for assistance with the electron microanalytical probe analyses and Prof. D. F. Shriver for the use of his resonance Raman facility. This work has been supported under the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR82-16972) and by National Science Foundation Grants DMR77-26409 (to B.M.H.) and CHE83-08076 (to J.A.I.).

**Registry No.** $[FeCl(pc)]_2I_2$, 95978-29-3; Fe(pc)I, 85962-26-1; Fe(pc), 132-16-1.

**Supplementary Material Available:** Figure 3, a stereoview of the unit cell of $[FeCl(pc)]_2I_2$, and Tables IIb (positions and anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom positions, and isotropic thermal parameters), III (root-mean-square amplitudes of vibration), IV (structure amplitudes for $[FeCl(pc)]_2I_2$), Vb (final positional and thermal parameters for all atoms), and VI (structure amplitudes for Fe(pc)I) (36 pages). Ordering information is given on any current masthead page.

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