A New Approach to Cofacially Assembled Partially Oxidized Metal Phthalocyanine Low Dimensional Solids: Synthesis, Structure, and Electrical Conductivity Properties of the Fe(IV) Containing Species $[(PcFe)_2C](I_3)_{0.66}$ Obtained by I_2 Doping of (μ-Carbido)bis[phthalocyaninatoiron(IV)]

A. M. Paoletti,[†] G. Pennesi,[†] G. Rossi,*[,†] and C. Ercolani*[,‡]

ICMAT (CNR), Area della Ricerca di Roma, C. P. 10, 00016 Monterotondo Stazione, Italy, and Dipartimento di Chimica, Università La Sapienza, p.le A. Moro 5, 00185 Roma, Italy

Received February 24, 1995[⊗]

Oxidation by iodine of the Fe(IV)−phthalocyanine μ-carbido complex $[PcFe]_2C$ (Pc = phthalocyaninato anion) leads to the species $[(PcFe)_2C](I_3)_{0.66}$ (**I**), whose structure consists of partially oxidized stacked $[(PcFe)_2C]^{+0.66}$ cations and parallel chains of I_3^- ions. Powder X-ray diffraction patterns of **I** indicate isomorphism with PcNiI and other known saltlike I_2 doped linearly elongated metal phthalocyanine derivatives, though different samples having different crystalline character are obtained, **Ia** and **Ib**, depending on the medium used for the preparation, i.e. benzene or chloronaphthalene, respectively. Mössbauer, EPR, and IR spectra confirm, in both **Ia** and **Ib**, the presence of Fe(IV) and the formation of the phthalocyanine π-cation radical, while Raman spectra give clear evidence of the presence of the totally symmetric I_3^- anion. IR spectra show also, both for **Ia** and **Ib**, the typical broad absorption normally present for highly electrically conducting systems. Crystalline character and IR spectral features are examined in connection with the observed electrical conductivity values obtained on pressed powders, i.e $(1.0 \pm 0.5) \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ (**Ia**) and $(0.5 \pm 0.5)\ \Omega^{-1}\ cm^{-1}$ (**Ib**). A relationship between structure and electrical conductivity is discussed in the light of the data already reported on related systems.

Introduction

In recent years an intensively growing number of partially oxidized metal phthalocyanine derivatives behaving as good electrically conductive systems has been reported.[1] Among these systems, particularly interesting are the I_2 doped, cofacially assembled, saltlike aggregates, obtained from simple metal phthalocyanine units, such as PcNi, or polymeric metalloxanes of formula $[M(Pc)O]_n$ (M = Si, Ge), and simplified as PcNiI (alternatively formulated as $PcNi(I_3)_{0.33}$)[2] and $([M(Pc)O]I_{1.1})_n$,[3] respectively. Common features of these doped materials are as follows: (a) ligand-centered oxidation, with the central metal ion experiencing in all cases oxidation states stable toward oxidation with I_2, i.e. Ni(II), Si(IV), Ge(IV); (b) attainment, by each Pc unit in the stacked polymer, of a nonintegral oxidation state, i.e. +0.33, or close to it; (c) associated presence of parallel chains of I_3^- ions; (d) electrical conductivity, σ_{RT}, measured on polycrystalline samples, in the range $0.1-1\ \Omega^{-1}\ cm^{-1}$. We recently reported that, even starting from quite different metal phthalocyanine precursors, i.e. the sandwich $[Pc_2Ti]$ (Ti^{+4}, d^0) ("stapled" by two inter-ligand C−C σ bonds),[4] and its Sn(IV) analog[4,5] ("unstapled"),[5] doping with iodine produces species of composition Pc_2MI_2 (M = Ti, Sn), for which X-ray analysis has shown[6] that they are isomorphous between themselves and with PcNiI. Hence, their correct formulation is $[Pc_2M](I_3)_{0.66}$ and their main features strictly follow points a−d, with only some difference (discussed below) for the σ_{RT} values. Taking into account that PcNiI, in turn, is isomorphous and practically isostructural with the metalloxane polymers $([M(Pc)O]I_{1.1})$,[3] it can be concluded that all the species considered are here strongly structurally interrelated (Figure 1).

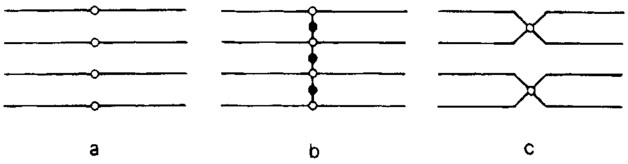

Figure 1. Schematic representation of iodine-doped phthalocyanine materials (chains of I_3^- ions neglected): (a) PcNiI; (b) $[M(Pc)OI_{1.1}]_n$ (M = Si, Ge); (c) Pc_2TiI_2.

We have been widely investigating single-atom bridged metal phthalocyanine complexes of formula PcM−X−MPc, M being mostly Fe,[7−9] but also Ru,[10] and X = O,[7] N,[8,10] all C.[9] Among them, μ-nitrido[8,10] and μ-carbido[9] species have: (i) a linear bridging M−X−M bond system because of the π-bonding flowing, through X, between the two metal centers, and (ii) the

---

[†] ICMAT (CNR).

[‡] Università La Sapienza.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

(1) (a) Schultz H.; Lehmann H.; Rein M.; Hanack, M. *Struct. Bonding* **1991**, *74*, 41−146; (b) Abbreviations used in the present paper: Pc = phthalocyaninato anion, $C_{32}H_{16}N_8^{2-}$; ClNP = α-chloronaphthalene; TPP = tetraphenylporphyrinato anion; py = pyridine, 4-mepy = 4-methylpyridine, pip = piperidine; 1-meim = 1-methylimidazole.

(2) 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.

(3) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schock, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551.

(4) Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1971.

(5) (a) Kroenke, W. J.; Kenney, M. E. *Inorg. Chem.* **1964**, *3*, 251. (b) Bennett, W. E.; Broberg, D. E.; Baezinger, N. C. *Inorg. Chem.* **1973**, *12*, 930.

(6) Capobianchi, A.; Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1993**, *32*, 4605.

(7) Ercolani, C.; Monacelli, F.; Dzugan, S.; Goedken, V. L.; Pennesi, G.; Rossi, G. *J. Chem. Soc., Dalton Trans.* **1991**, 1309, and references therein.

(8) Ercolani, C.; Gardini, M.; Pennesi, G.; Rossi, G.; Russo, U. *Inorg. Chem.* **1988**, *27*, 422, and references therein.

(9) (a) Ercolani, C.; Gardini, M.; Goedken, V. L.; Pennesi, G.; Rossi, G.; Russo, U.; Zanonato, P. *Inorg. Chem.* **1989**, *28*, 3097. (b) Rossi, G.; Goedken, V. L.; Ercolani, C. *J. Chem. Soc., Chem. Commun.* **1988**, 46.

(10) Rossi, G.; Gardini, M.; Pennesi, G.; Ercolani, C.; Goedken, V. L. *J. Chem. Soc., Dalton Trans.* **1989**, 193.

0020-1669/95/1334-4780$09.00/0

two cofacially joined Pc units, closely approaching to one another (*ca.* 3.4 Å) and minimizing inter-ring steric and electronic repulsion by relative rotation to a *quasi*-staggered position. With these features in mind, we thought that selected X-bridged species might be used as appropriate precursors, as an additional choice to the examples already reported,[2-4] for the synthesis, by I_2 doping, of stacked saltlike systems with enhanced electrical conductivity properties. Among the above species, the μ-carbido dimer $[PcFe]_2C$[9] was selected, as both metal centers in it are in the unusual +4 oxidation state, certainly stable toward I_2 oxidation. In addition, some structural information can be derived for it from its 1-meim adduct, i.e. $\{[(1\text{-meim})PcFe]_2C\}$, present in the crystals of $\{[(1\text{-meim})PcFe]_2C\}.[PcFe(1\text{-meim})_2].3Me_2CO$, whose the structure has been elucidated by single-crystal X-ray work.[9b] The present contribution illustrates the synthesis, chemical physical characterization, and electrical conductivity properties of the species $[(PcFe)_2C](I_3)_{0.66}$, obtained by I_2 doping of $[PcFe]_2C$.

Experimental Section

PcFe was purchased from Eastman Kodak, and eventually purified by sublimation under vacuum (400 °C, 10^{-2} mmHg). CI_4 was obtained as previously reported.[11] I_2 was a bisublimed material. PcNiI and Pc_2TiI_2 were prepared according to the methods previously reported.[2,6] All chemicals were reagents grade. Solvents were spectrometric grade, purified by distillation when necessary.

Synthesis of $(PcFe)_2C$. This compound was prepared from PcFe and CI_4 in presence of sodium dithionite as previously described.[9b] Even if purified by convertion into its 1-meim adduct, followed by elimination of 1-meim by heating under vacuum,[9a] $(PcFe)_2C$ still contains some unreacted PcFe as impurity, as can be easily proved by solution visible spectra in pyridine. These spectra show the presence of a strong absorption at 620 nm,[9b] due to the μ-carbido adduct $[(py)PcFe]_2C$, accompanied by a shoulder, located at 653 nm, typical of $PcFe(py)_2$. The presence of this latter (5–8%), obviously formed from PcFe, can be estimated quantitatively in the various samples handled by its known ϵ value.[12]

Oxidation of $(PcFe)_2C$ with I_2 in Benzene. Finely ground $(PcFe)_2C$ (100 mg, 0.087 mmol) was suspended in a benzene solution (8–10 mL) of I_2 (200 mg, 0.79 mmol). The mixture was kept under stirring at room temperature for 12 h. Shorter reaction times sometimes determine only a partial convertion into the oxidized species. The solid was filtered and washed abundantly with benzene until the latter was colorless, then the solid was dried under vacuum. Yields are above 90%. Anal. Calcd for the formula $[(PcFe)_2C](I_3)_{0.66}$, $C_{65}H_{32}N_{16}Fe_2I_2$: C, 55.66; H, 2.28; N, 15.97; I, 18.09. Found: C, 54.95; H, 2.16; N, 15.54; I, 17.35. The dark greenish microcrystalline material obtained is indefinitely stable to air. It is practically insoluble in most organic nondonor solvents and in water.

Oxidation of $(PcFe)_2C$ with I_2 in ClNP. Finely ground $(PcFe)_2C$ (120 mg, 0.104 mmol) was suspended (partially dissolved) in ClNP (12 mL); to the suspension was added an excess of I_2 (120 mg, 0.473 mmol). The mixture was heated at 60–70 °C for 1 h. After cooling and filtration, the solid was washed with ethanol until the latter was colorless. The solid was then dried under vacuum. Yields approach 100%. Anal. Calcd: C, 55.66; H, 2.28; N, 15.97; I, 18.09. Found: C, 55.17; H, 2.29; N, 15.35; I, 17.58.

Physical Measurements. IR spectra were recorded in the region 4000–200 cm^{-1} on a Perkin-Elmer 983 instrument by using Nujol mulls between CsI disks. X-band EPR low temperature (80 K) measurements were run on a Varian E-109 spectrometer; the field was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH). Conventional powder X-ray diffraction patterns were recorded on a Seifert 3000 instrument with a Cu Kα radiation (50 kV/30 mA). Elemental analyses were provided by the Servizio di Microanalisi at the Area della Ricerca (CNR). Thermogravimetric data were obtained by a Du Pont 950 analyzer under a stream of N_2 (0.5 L/min). Dc conductivity measurements were performed at room temperature by the four-probe technique using powder pellets 1.0 cm (diameter), pressed at ca. 10^8 Pa. Raman spectra were recorded on a Bruker RFS 100 FT-Raman spectrometer, operating with an exciting frequency at 1064 nm (Nd:YAG laser). Power levels of laser source varied from 10 to 100 mW. The detection of the signal was made with an indium–gallium–arsenide detector operating at room temperature. The samples, in the form of powders, were packed into a suitable cell and then fitted into the compartment designed for use 180° scattering. The high intensity excitation source causes local overheating and decomposition of the samples was observed. The use of a glass capillary as container of the powder was sufficient to reduce decomposition. Raman spectra could also be run on a Spex triplemate Model 1454 OMA detector. The exciting radiation, focused on a 5 mm Pyrex holder spinning at 1200 rpm, was provided by the 480 nm line of a Coherent Model Innove 90 argon ion laser. The two instruments gave identical spectra. Mössbauer spectra were run as previously reported.[8]

Results and Discussion

$[PcFe]_2C$ is a Fe(IV) μ-C-bridged species stable to air. By contact with N-bases it gives its corresponding bis-adducts of formula $[(N\text{-base})PcFe]_2C$ (N-base = py, 4-mepy, pip, 1-meim).[9a] The structure of the 1-meim adduct[9b] shows that the Fe–C–Fe bridge is practically linear (178°), with Fe–C bond distances of 1.69 Å and the Fe atoms, six-coordinated, and located in the center of the respective N_4 macrocyclic chromophore. Reasonably, the absence in $[PcFe]_2C$ of ligands coordinated at the external axial positions should reinforce and, hence, shorten the Fe–C bonds of the Fe–C–Fe bridge, with an implied displacement of the five-coordinate Fe centers out-of-plane, toward the bridging C atom, as occurs in the analogous μ-carbido species $[(TPP)Fe]_2C$.[13]

Reaction of $[PcFe]_2C$ with I_2, either in benzene or ClNP, determines partial oxidation of the μ-carbido species and systematically leads to materials of identical composition which are in keeping with the formulation $[(PcFe)_2C](I_3)_{0.66}$ (**I**). Thermal treatment of **I**, or its dissolution in pyridine, reverse the process, forming $[PcFe]_2C$ or its bis adduct $[(py)PcFe]_2C$, respectively.

Samples of **I** obtained from benzene (**Ia**) or ClNP (**Ib**) show identical powder X-ray diffraction patterns as to the number, position, and relative intensity of peaks present; however, the spectra of samples of **Ia** reveal, reproducibly, a lower crystalline character than those of **Ib**. *Most importantly*, comparison of the X-ray diffraction pattern of **Ib** with those of the two species PcNiI and Pc_2TiI_2, already unequivocally established to be isomorphous between themselves from single crystal X-ray work,[2,6] indicates striking similarity (see Figure 2, and data in Table 1), suggesting practical isomorphism of **Ib** with the Ni and Ti species. This isomorphism is, in turn, extended, through PcNiI, to the species $([M(Pc)O]I_{1.1})$ (M = Si(IV), Ge(IV)).[3] From these data, the straightforward consequence is the assignment to **I** (either **Ib** or **Ia**) of a solid-state structure which consists of stacks of positively charged μ-carbido fragments and parallel chains of I_3^- counterions. As we show below, all additional information at hand for **I** strongly supports the assignment made.

The low temperature Mössbauer spectrum of **Ib** is given in Figure 3 (a similar spectrum is shown by **Ia**). The spectrum shows the presence of one intense well defined doublet, with δ and ΔE_Q values of −0.09 mm/s and 2.62 mm/s, respectively. These parameters are listed in Table 2, together with those of related species. The observed values for **Ib** are only slightly

---

(11) McArthur, R. E.; Simons, J. H. *Inorg. Synth.* **1950**, *3*, 37.

(12) (a) Dale, B. W. *Trans. Faraday Soc.* **1969**, *65*, 331. (b) Monacelli, F. *J. Chem. Soc. Dalton Trans.* **1991**, 3373.

(13) Goedken, V. L.; Deakin, M. R.; Bottomley, L. A. *J. Chem. Soc., Chem. Commun.* **1984**, 607.

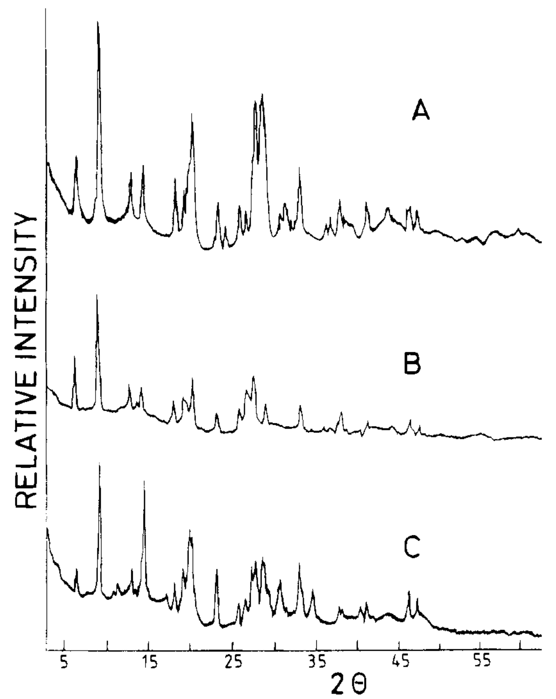

Figure 2. X-ray powder diffraction patterns of PcNiI (A), **Ib** (B), and Pc_2TiI_2 (C). Pattern A appears to be identical to that reported previously for the same species.[3]

Table 1. Powder X-ray Diffraction Patterns of **Ib** and Related Substances[a]

	d_{exp} (I_{max})		
no.	PcNiI	**Ib**	Pc_2TiI_2
1	13.99 (40.8)	13.85 (47.4)	*13.9*
2	9.83 (98.2)	9.80 (90.0)	9.85 (63.7)
3	6.94 (35.0)	6.94 (37.9)	*6.94* (?)
4	6.22 (37.7)	6.21 (36.3)	6.22 (59.2)
5	4.91 (33.2)	4.92 (28.3)	4.92 (25.1)
6	*4.65*	*4.65*	*4.65*
7	4.42 (55.8)	4.38 (42.9)	4.47 (43.4)
8	3.85 (25.4)	3.86 (21.0)	3.86 (29.7)
9	3.49 (22.6)	*3.49* (?)	*3.49*
10	*3.39*	*3.39*	*3.39*
11	3.29 (32.1)	3.27 (44.3)	3.29 (22.5)
12	3.24 (59.0)		3.23 (32.8)
13	3.14 (61.8)	3.11 (27.7)	3.14 (34.3)
14	*2.90*		2.95 (20.7)
15	2.73 (36.8)	2.73 (27.8)	2.73 (32.7)
16			2.60 (22.8)
17	2.38 (25.9)	2.38 (27.8)	*2.38*
18	2.21 (25.1)	2.20 (18.3)	2.20 (19.2)
19	2.07 (23.6)		
20	1.97 (23.9)	1.97 (20.3)	1.97 (23.0)

[a] The d_{exp} data in italics were not estimated by the instrument and were evaluated visually.

different from those observed for the corresponding Fe(IV) precursor. The δ value for **Ib** is less negative than that of $[PcFe]_2C$[9a] and is hence shifted in a direction opposite to that expected in case of further, though highly improbable, metal-centered oxidation. Moreover, the value is close to that of the hexafluorophosphate Fe(IV) μ-N dimer,[8] far from that of $[PcFe(III^1/_2)]_2N$,[8,14] and definitely well in the range expected for Fe(IV) species.[15] This result definitely excludes any significant involvement of the Fe centers in the redox process associated with the I_2 doping.

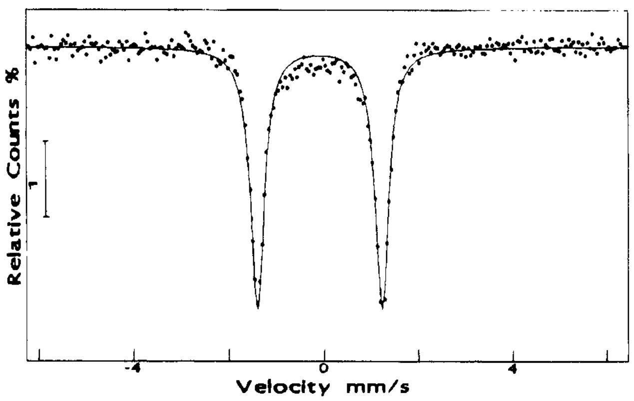

Figure 3. Low temperature (80 K) Mössbauer spectrum of **Ib**.

Table 2. Mössbauer, Structural, and Electrical Conductivity Data of **I** and Related Species

compound	δ,[a] mm/s)	ΔE_Q, mm/s	Γ,[b] mm/s	irs,[c] Å	σ_{RT},[d] $\Omega^{-1}cm^{-1}$	ref
Ia	−0.09	2.62	0.17	?	$(1.0 \pm 0.5).10^{-2}$	*e*
Ib	−0.09	2.62	0.17	?	(0.5 ± 0.5)	*e*
$[PcFe(IV)]_2C$	−0.16	2.69	0.11			9, *e*
$\{[PcFe(IV)]_2N\}(PF_6)$	−0.10	2.06	0.16			8
$[PcFe(III^1/_2)]_2N$	0.18	1.08	0.19			8
PcNiI				3.244	0.7	2
$[(PcSiO)I_{1.1}]$				3.30	0.58	3
$[(PcGeO)I_{1.1}]$				3.48	0.11	3
Pc_2TiI_2				3.19	$(0.5-5).10^{-3}$	6
Pc_2SnI_2				?	$(0.5-5).10^{-2}$	6

[a] Quoted relative to Fe metal. [b] Half-width at half-maximum height. [c] Irs = Inter-ring spacing. [d] Measured on polycrystalline pressed pellets. Data reported for **Ia** and **Ib** were obtained from measurements on several samples, as was also the case for Pc_2TiI_2 and Pc_2SnI_2.[6] [e] This paper.

EPR spectra of samples of **Ia** and **Ib** show similar features. Single isotropic narrow peaks of comparable intensity, and located in the position of the free electron value ($g = 2.003$), are observed in both cases. The intensity of these peaks is comparable to that measured, under similar registration conditions, for the I_2-doped Ti(IV) material, i.e. Pc_2TiI_2.[6] These data exclude the possibility that paramagnetic impurities, always present in phthalocyanine materials, might be assumed as exclusively responsible for the observed EPR spectrum. Instead, they strongly indicate that the doping process has determined the formation of the Pc π-cation radical on both **Ia** and **Ib**.

The Raman spectrum of **I** (**Ia** or **Ib**, see for the latter the spectrum shown in Figure 4) gives clear evidence of the presence of a totally symmetric I_3^- ion, as is shown by the detection of an intense absorption at 107 cm^{-1}, accompanied by the expected associated overtones at 211 and 319 cm^{-1}. Thus, the Raman spectrum must be taken as indicative of the saltlike nature of **I**, in keeping with the formulation given.

Samples of both **Ia** and **Ib** show IR spectra which are characterized by the presence of a broad absorption spreading in the region 4000−1000 cm^{-1}, observed for other partially oxidized phthalocyanine derivatives,[2,3,5] and typical of highly electrically conducting systems. For samples of **Ia** the broad absorption shows its maximum intensity roughly located above 3000 cm^{-1} (Figure 5A). In this case, although affected in intensity, all the spectrum below 1600 cm^{-1}, normally showing the Pc skeleton modes, is clearly visible. In this region, the Fe−C−Fe bond medium-to-strong mode, present at 990 cm^{-1}

---

(14) Bottomley, L. A.; Gorce, J.-Noel; Goedken, V. L.; Ercolani, C. *Inorg. Chem.* **1985**, *24*, 3733.

(15) Ercolani C. and Floris B. Metal Phthalocyanine Single-Atom Bridged Dimers. In *Phthalocyanines—Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH Publishers: New York, 1993; Vol. 2, Chapter 1, pp 1−41.

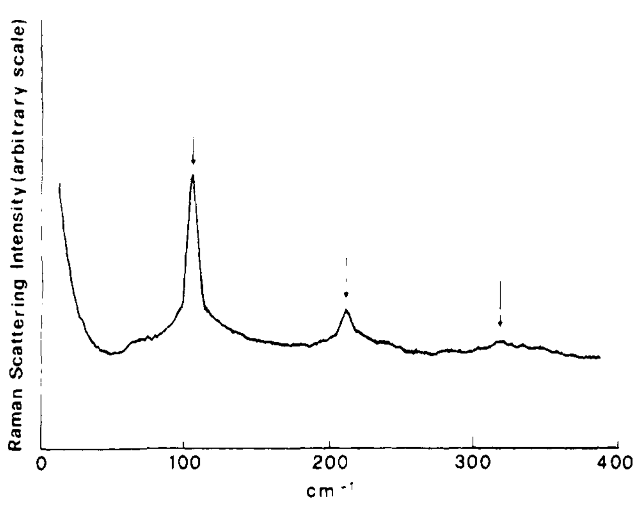

Figure 4. Room temperature Raman spectrum of **Ib**.

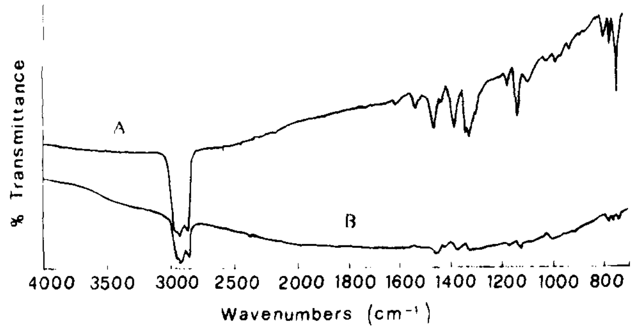

Figure 5. IR spectra of **Ia** (A) and **Ib** (B).

in $[PcFe]_2C$,[9b] has completely disappeared. This reproducibly happens in totally oxidized samples; hence, eventually, its residual presence for I_2-doped samples can be taken as indicative of incomplete oxidation. Two new absorptions appear at 1120 and 1320 cm^{-1}, the first one being located in the region where bands attributable to the presence of Pc π-cation radicals are normally observed.[16] Even more drastic changes appear in the IR spectrum of samples of **Ib** (Figure 5B): (a) the broad absorption invades practically all the region explored with its maximum shifted to lower frequencies and centered roughly at 1600 cm^{-1}; (b) the Pc skeletal modes are almost completely obscured; as far as they can be detected, however, they do not differ from those observed for samples of **Ia**. The spectral features in point b are more closely of the type encountered for the electrically conductive materials reported in Figure 1.[2,3,6]

Pressed pellets of powdered samples of both **Ia** and **Ib** show, as expected, electrical conduction properties. Samples of the less crystalline **Ia** are reproducibly less conductive than samples of **Ib**. For this latter the σ_{RT} value is $(0.5 \pm 0.5)\ \Omega^{-1}\ cm^{-1}$; that of **Ia**, instead, is $(1.0 \pm 0.5) \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. The different crystalline character of **Ia** and **Ib** must certainly affect the conductivity and can, at least partly, account for the observed different values measured, i.e. the more the crystalline character for **Ib**, the higher its electrical conductivity value. A further observation refers to a probable connection between electrical conductivity and position of the broad exciton band in the IR spectrum. In a number of species,[17,18] in fact, it has been shown that an increase in electrical conductivity is clearly correlated to a shift of the broad IR absorption toward lower frequencies. This is, indeed, also the case for samples of **Ia** and **Ib**.

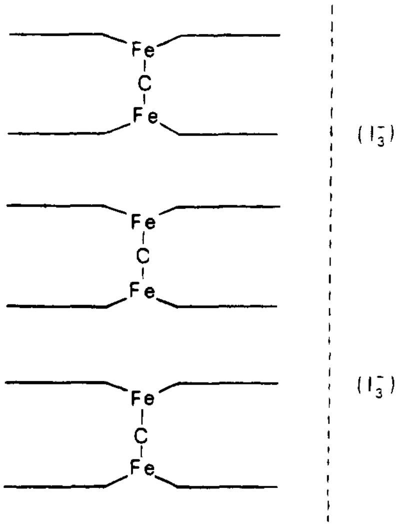

Figure 6. Proposed structure for **I**.

The proposed structural arrangement for **I**, closely approaching those given in Figure 1, is shown schematically in Figure 6. The cofacial assembly of the Pc rings, essential for the π-electron transport through the stacked units, very likely implies, for the μ-carbido units, unequal internal and adjacent inter-ring spacings, as occurs in the Ti and Sn sandwiched species,[6] but differently from the cases of the Ni, Si, and Ge materials.[2,3] The array present in **I** should also imply, as found elsewhere,[2,3,6] a *quasi*-staggered position of adjacent Pc rings, which facilitates their relative approach.

The following list of materials in order of decreasing conductivity is offered by the data summarized in Table 2 (inter-ring spacings between adjacent Pc units are given in parentheses): PcNiI (3.244 Å) ~ **Ib** (?) ~ ($[Si(Pc)O]I_{1.1}$) (3.30 Å) > ($[Ge(Pc)O]I_{1.1}$) (3.48 Å) > Pc_2SnI_2 (?) > Pc_2TiI_2 (3.19 Å, average value). Thus, **Ib** is among the most conducting members of the series, behaving far better than the sandwiched Pc_2SnI_2 and Pc_2TiI_2. Undoubtedly, the degree of departure from planarity of the Pc macrocycles in these species is one of the major factors affecting the efficiency of the inter-unit charge transfer along the columnar stacks, and, hence, the electrical conductivity. In the case of Pc_2TiI_2, in fact, the lowest observed σ_{RT} value, clearly in contrast with its shortest measured average inter-ring spacing, has been previously[6] correlated with the residual high Pc ring distortion, still reminiscent of the "stapled", extraordinarily distorted arrangement caused by the two inter-ligand C−C σ-bonds present in $[Pc_2Ti]$.[4] Pc_2SnI_2 is strictly isomorphous with Pc_2TiI_2[6] but not necessarily isostructural since it originated from an "unstapled" precursor. Thus, the departure from planarity of the Pc fragments in Pc_2SnI_2 should be less marked, this justifying the observed slight increase of its conductivity value. In **Ib**, the presence of a triatomic bridge (Fe−C−Fe) between the two Pc fragments of the μ-carbido unit should determine a considerable release of strain, since the length of the Fe−C−Fe bridge can be estimated not to fall below 3.30 Å, as supported by previous single crystal X-ray work on $[(1\text{-meim})PcFe]_2C$[9b] and $[(TPP)Fe]_2C$.[13] Thus, although deviation from planarity of the Pc rings certainly persists as a consequence of the out-of-plane displacement of the five-coordinate Fe centers toward the central carbon atom, less marked ligand distortion than in the Ti and Sn sandwiched materials is expected for **Ib**, this making the structural features of this material very close to those present in the stacked

---

[16] Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. *Inorg. Chem.* **1975**, *14*, 461.

[17] Perez-Albuerne, E. A.; Johnson, H., Jr.; Trevoy, D. J. *J. Chem. Phys.* **1971**, *55*, 1547.

[18] Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.

($[M(Pc)O]I_{1.1})_n$ species, thus allowing the raising of σ_{RT} to the highest values.

The presence of PcFe as an impurity (5–8%) in $[PcFe]_2C$ needs to be briefly considered as to the possible effects produced, upon iodine doping, on the σ_{RT} values for **I**. The reaction conditions used for the synthesis of **I** recall closely those used elsewhere[19] for the reaction of PcFe with I_2 in ClNP. This reaction is intriguing, since, fairly irreproducibly, it leads, mainly, to the formation of two species, i.e. $[PcFeCl]_2I_2$ and PcFeI, whose the structures have been both elucidated by single-crystal X-ray work.[19] While $[PcFeCl]_2I_2$ is very likely a non conducting system, conductivity measurements[19] on a single crystal of PcFeI, found to be isostructural with PcNiI with only a larger interspace among adjacent Pc units along the stacking direction, gave a σ_{RT} value of 20 Ω^{-1} cm^{-1}. If the difference in the electrical conductivity normally observed for a single crystal and that of the same material used as polycrystalline pressed pellets is considered, a σ_{RT} value of 0.2–0.02 Ω^{-1} cm^{-1} is predicted for polycrystalline PcFeI and, hence, a value close to that found for **Ib** or lower. In experiments carried out by us under the experimental conditions used for **I**, PcFe and I_2 gave a reaction material, whose the powder X-ray diffraction pattern shows all the most intense peaks expected for PcFeI, roughly indicating that this species is preponderantly present, and additional peaks revealing the presence of at least one more species. The elemental analysis on this material shows an iodine content higher than that expected for PcFeI. The measured electrical conductivity of the bulk material, average of two experiments, is $(2 \pm 0.3) \times 10^{-2}$ Ω^{-1} cm^{-1}, several orders of magnitude higher than that of PcFe ($<10^{-8}$ Ω^{-1} cm^{-1}), confirming expectation. Nevertheless, this conductivity value is definitely lower than that of **I**. This indicates that the contaminants present in **I**, were they either PcFeI or (PcFeCl)-I_2, could not significantly affect its σ_{RT} value, or, just in case, they would tend to lower the observed value. Elemental analyses, X-ray powder diffraction patterns, Raman, and IR spectra did not give evidence of traces of any specific contaminant present. Only the Mössbauer spectrum (Figure 3) shows at the base of the main doublet some evidence of the presence of small amounts of impurities, hard, however, to be identified, from the broad trace of the baseline.

The new case of electrically conductive phthalocyanine material presented here, **I**, further demonstrates that a I_2 doped monodimensional array is made possible, provided that the precursors either do not preclude cofacial assembly, as for PcNi, or they do realize it as unitary components, as for Pc_2M (M = Ti(IV), Sn(IV)) and $[Pc_2Fe]_2C$, or as stacked polymers, as is the case for the species ($[M(Pc)O]I_{1.1}$). In this context, a minor role, whatever it might be, seems to be played in the charge transport by the metal centers. This appeared definitely clear for the sandwiched Ti(IV)- and Sn(IV)-doped species,[6] in which the metal centers are trapped in between the two Pc units, with no chance of significant participation to the delocalization of charge along the stacking direction. A similar situation, although less marked, very likely occurs in **I**, because of the "internal" location of the two Fe centers.

All our efforts to prepare single crystals of **I**, either by determining slow contact of solutions of $[(PcFe)_2C]$ and I_2 or by electrocrystallization techniques, have been so far unsuccessful. In case of future success, it is in our mind to develop as well refined methods of further purification of **I** and eventually verify an improvement of its electrical conductivity properties, as has been indeed the case, recently, for highly pure PcNiI.[20]

Acknowledgment. We thank Prof. P. Deplano (University of Cagliari) and Dr. G. Mattei (IMAI, CNR) for help with the Raman spectra and useful discussions. We also thank Prof. U. Russo for the run of Mössbauer spectra. Elemental analyses in the Area della Ricerca (CNR) were performed by L. Petrilli and F. Dianetti. We acknowledge financial support by the Italian Consiglio Nazionale delle Ricerche.

IC950216F

---

(19) Palmer, S. A.; Stanton J. L.; Jaggi, N. K., Hoffman, B. M.; Ibers, J. A.; Shwartz L. H. *Inorg. Chem.* **1985**, *24*, 2040.

(20) Thompson, J. A.; Murata, K.; Miller, D. C.; Stanton, J. L.; Broderick, W. E.; Hoffman, B. M.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 3456.