

Interligand C–C σ -Bond Breaking and Repair in a “Stapled” Bis(phthalocyaninato)titanium Complex. Synthesis, Characterization, and Electrical Conductivity Properties of Oxidation Products of Bis(phthalocyaninato)titanium(IV) and Bis(phthalocyaninato)tin(IV) and X-ray Crystal Structure of $[\text{Pc}_2\text{Ti}](\text{I}_3)_{0.66}$

A. Capobianchi,[†] C. Ercolani,^{*‡} A. M. Paoletti,[†] G. Pennesi,[†] G. Rossi,^{*†} A. Chiesi-Villa,[§] and C. Rizzoli[§]

ICMAT (CNR), Area della Ricerca di Roma, Monterotondo Stazione, Roma, Italy, Dipartimento di Chimica, Università degli Studi di Roma “La Sapienza”, Roma, Italy, and Istituto di Strutturistica Chimica, Università di Parma, Parma, Italy

Received November 13, 1992[⊙]

Oxidation reactions of bis(phthalocyaninato)titanium(IV), Pc_2Ti , and bis(phthalocyaninato)tin(IV), Pc_2Sn , with I_2 and HNO_3 lead to the formation of the species $[\text{Pc}_2\text{M}](\text{I}_3)_{0.66}$ and $[\text{Pc}_2\text{M}]\text{NO}_3$, respectively [$\text{M} = \text{Ti}(\text{IV})$, $\text{Sn}(\text{IV})$]. Exchange of the NO_3^- group with PF_6^- leads to the species $[\text{Pc}_2\text{M}]\text{PF}_6$. Reduction of these oxidized saltlike species with NaBH_4 results in the formation of the respective precursors Pc_2Ti and Pc_2Sn . The structure of the complex $[\text{Pc}_2\text{Ti}](\text{I}_3)_{0.66}$ has been elucidated by a low-temperature (-160°C) single-crystal X-ray study. The complex crystallizes in the tetragonal system. Unit cell data: formula $\text{C}_{64}\text{H}_{32}\text{I}_2\text{N}_{16}\text{Ti}$, $M = 1326.8$, $a = b = 13.841(3) \text{ \AA}$, $c = 6.370(3) \text{ \AA}$, $V = 1220.3(7) \text{ \AA}^3$, $Z = 1$, space group $P4/mcc$. The structure of $[\text{Pc}_2\text{Ti}](\text{I}_3)_{0.66}$ shows columnar stacks of nonintegrally positively charged $[\text{Pc}_2\text{Ti}]^{0.66+}$ units and parallel chains of iodine atoms consisting of I_3^- units. In the “sandwiched” unit (a) the two interligand C–C σ bonds observed in Pc_2Ti are no longer present, the new corresponding C–C distance being 2.839 \AA , (b) the two Pc groups are staggered at an angle of 41.1° , (c) as in the precursor Pc_2Ti , the titanium atom is surrounded by the eight inner nitrogen atoms in the form of a square antiprism, with Ti–N bond distances of $2.246(7) \text{ \AA}$, and (d) the distance between the two N_4 planes is 2.42 \AA , which implies a distance of 1.21 \AA of Ti to the center of its adjacent N_4 plane. Solid crystalline $[\text{Pc}_2\text{Sn}](\text{I}_3)_{0.66}$ is isostructural with its Ti analogue. The nitrate and hexafluorophosphate derivatives are obtained as amorphous materials. Dc electrical conductivity of all the doped materials was measured on powdered compressed samples by Van der Pauw's method, and the values obtained are discussed in the light of the available crystallographic information, data from IR, resonance Raman, UV–visible, and EPR spectra, and thermogravimetric analysis. A possible explanation is provided for the higher electrical conductivity observed for the Sn complexes compared to that of the Ti complexes.

Introduction

A number of monomeric or polymeric oxygen atom-bridged metal phthalocyanines can be doped with iodine or other oxidizing agents, forming solid-state materials which behave as electrical conductors or semiconductors.¹ Basically, this behavior is strictly connected with the structural and electronic features of the fairly rigid square planar metal phthalocyanine framework, which is the site of extensive π -electron delocalization. In doped phthalocyanine materials, cofacial assembly of nonintegrally positively charged metal phthalocyanine units produces monodimensional aggregates which run parallel to the chains of appropriate counterions. The structural arrangement is often such that electron charge transfer is made possible along the chains, the efficiency of charge flow, and, hence, the measured electrical conductivity, depending upon the role played by the central metal ion, the organic macrocycle, and the selected anion.

There appear to be no cases so far reported in the literature of the synthesis and characterization of “partially oxidized” metal

bis(phthalocyanine) complexes, i.e. Pc_2M ($\text{Pc} = \text{phthalocyaninato}$ anion, $\text{C}_{32}\text{H}_{16}\text{N}_8^{2-}$), despite of the fact that these molecules recently received much attention, especially because of their synthetic and structural aspects,^{2–13} spectral properties,^{14–18} electrochromic behavior,^{13,19,20,21f} and electrical conductivity

[†] ICMAT (CNR).

[‡] Università “La Sapienza”.

[§] Università di Parma.

[⊙] Abstract published in *Advance ACS Abstracts*, August 15, 1993.

- (1) (a) 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. (b) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551. (c) Yakushi, K.; Sakuda, M.; Kuroda, H.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1986**, 1161. (d) Inabe, T.; Gaudtello, J. G.; Moguel, M. K.; Lyding, J. W.; Burton, R. L.; McCarthy, W. J.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7595. (e) Almeida, M.; Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J.; Marcy, H. O.; McCarthy, W. J.; Kannewurf, C. R. *Solid State Commun.* **1987**, *63*, 457.

- (2) Barrett, P. A.; Dent, C. E.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1719.
 (3) Kroenke, W. J.; Kenney, M. E. *Inorg. Chem.* **1964**, *3*, 251–254.
 (4) Gieren, A.; Hoppe, W. *Chem. Commun.* **1971**, 413.
 (5) Bennett, W. E.; Broberg, D. E.; Baezinger, N. C. *Inorg. Chem.* **1973**, *12*, 930.
 (6) Kasuga, K.; Tsutsui, M.; Petterson, R. C.; Tatsumi, K.; Van Opendbosch, N.; Pepe, G.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 4836.
 (7) De Cian, A.; Moussavi, M.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1985**, *24*, 3162.
 (8) Clarisse, C.; Riou, M. T. *Inorg. Chim. Acta* **1987**, *130*, 139.
 (9) Girolami, G. S.; Milam, S. N.; Suslick, K. S. *Inorg. Chem.* **1987**, *26*, 343.
 (10) Zhang, W. P.; Kuo, K. H.; Hou, Y. F.; Ni, J. Z. *J. Solid State Chem.* **1988**, *74*, 239.
 (11) Lachkar, M.; De Cian, A.; Fischer, J.; Weiss, R. *New J. Chem.* **1988**, *12*, 729.
 (12) Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1971.
 (13) Silver, J.; Lukes, P.; Howe, S. D.; Howlin, B. *J. Mater. Chem.* **1991**, *1*, 33.
 (14) Kroenke, W. J.; Kenney, M. E. *Inorg. Chem.* **1964**, *3*, 696.
 (15) (a) Kasuga, K.; Ando, M.; Morimoto, H. *Inorg. Chim. Acta* **1986**, *112*, 99. (b) Kasuga, K.; Morimoto, H.; Atarashi, H.; Isa, M. *Inorg. Chim. Acta* **1986**, *118*, L39. (c) Kasuga, K.; Atarashi, H. *Chem. Lett.* **1986**, 1679–1680. (d) Kasuga, K.; Morimoto, H. *Inorg. Chim. Acta* **1986**, *119*, L17.
 (16) Markovitsi, D.; Tran-Thi, T.-H.; Even, R.; Simon, J. *Chem. Phys. Lett.* **1987**, *137*, 107.
 (17) Bilsel, O.; Rodriguez, J.; Holten, D.; Girolami, G. S.; Milam, S. N.; Suslick, K. S. *J. Am. Chem. Soc.* **1990**, *112*, 4075.
 (18) Duchowski, J. K.; Bocian, D. F. *J. Am. Chem. Soc.* **1990**, *112*, 3312.

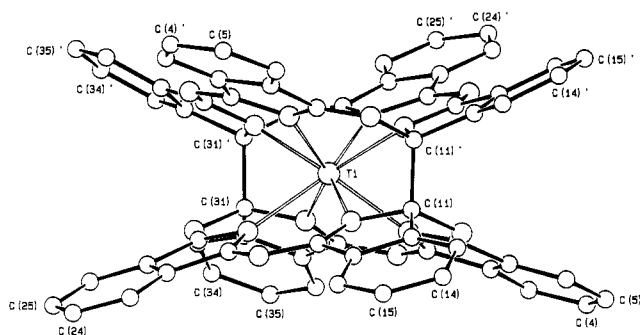


Figure 1. X-ray crystal structure of Pc_2Ti . Reprinted from ref 12 with permission. Copyright 1990 Royal Society of Chemistry.

properties.²¹ Difficulties with these sandwich-type molecules regarding good conductivity properties may be due to the "internal" position of the central metal, this certainly limiting or excluding the possibility of its active role in interunit charge transfer. Secondly, the binding strength displayed by the central metal ion on the ligated Pc residues may significantly remove the planarity of these latter, somewhat affecting the π -electron delocalization in the macrocyclic framework and the efficient cofacial approach in intermolecular association, a prerequisite for good conductivity contacts in the construction of linearly elongated molecular systems.

We recently reported on bis(phthalocyaninato)titanium(IV), Pc_2Ti (Figure 1), a sandwich-type molecule "stapled" by two interligand C–C σ bonds.¹² The arrangement of the metal bis(phthalocyanine) units in the crystal of Pc_2Ti is such that intermolecular contacts are well above the van der Waals distances ($>3.4 \text{ \AA}$); thus, Pc_2Ti behaves as an insulator. We also observed¹² that oxidation of Pc_2Ti with HNO_3 , which leads to the formation of $[\text{Pc}_2\text{Ti}]\text{NO}_3$, increases the values of the electrical conductivity.¹² In the present study, we report on the materials obtained by oxidation of Pc_2Ti and Pc_2Sn with I_2 and HNO_3 . A few new products have also been prepared which contain the PF_6^- counterion. The structural and electronic features of all these oxidized species are examined here in an attempt to achieve a better understanding of their improved electrical conductivity properties with respect to that of their precursors Pc_2Ti and $\text{Pc}_2\text{-Sn}$.

Experimental Section

Pc_2Ti -CINP (CINP = α -chloronaphthalene) and β - Pc_2Sn -CINP were obtained as previously described.^{3,12}

$[\text{Pc}_2\text{Ti}](\text{I}_3)_{0.66}$ (Hereafter Indicated as Pc_2TiI_2). This compound was prepared in different media.

(a) **In Benzene.** Pc_2Ti -CINP (200 mg, 0.16 mmol) was suspended in a solution of I_2 (200 mg, 0.78 mmol) in benzene (5 mL). The suspension was stirred at room temperature for 2 h. After filtration, the solid material was washed with benzene to eliminate excess I_2 and dried under vacuum (205 mg, 96.5% yield). Anal. Calcd for Pc_2TiI_2 , $\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{Ti}$: C, 57.95; H, 2.41; N, 16.89; I, 19.13. Found: C, 57.32; H, 2.40; N, 16.19; I, 20.59. The greenish-black complex has a low crystalline character.

(b) **In CINP.** A solution of I_2 (200 mg, 0.78 mmol) in CINP (5 mL) was added at room temperature to a solution of Pc_2Ti -CINP (200 mg, 0.16 mmol) in hot (80 °C) CINP (7 mL); after 2 h of stirring, the solid

crystalline greenish product formed was isolated by filtration, washed with benzene, and dried under vacuum (202 mg, 95% yield).

Single crystals of Pc_2TiI_2 were obtained by slow diffusion at room temperature of a solution of the Ti complex in CINP (10^{-3} M) into a solution of I_2 in the same medium. Small prismatic crystals, having approximate dimensions of $0.1 \times 0.1 \times 0.1 \text{ mm}$, were formed in a week or so. Attempts were made for the preparation of single crystals by the electrocrystallization technique in CINP. Normally, too small and fragile needles were formed, unsuitable for X-ray work.

$[\text{Pc}_2\text{Sn}](\text{I}_3)_{0.66}$ (Hereafter Indicated as Pc_2SnI_2). This complex can be obtained by methods very similar to those used for the synthesis of the corresponding Ti complex. The preparation in CINP in presence of an excess of I_2 is performed at 40–50 °C because of the low solubility of Pc_2Sn in that medium. The reaction is normally completed in 2 h. Anal. Calcd for Pc_2SnI_2 , $\text{C}_{64}\text{H}_{32}\text{N}_{16}\text{I}_2\text{Sn}$: C, 55.01; H, 2.29; N, 16.03; I, 18.16. Found: C, 54.26; H, 2.27; N, 15.09; I, 18.59. Attempts to prepare crystals of this Sn–iodine species suitable for X-ray work by the diffusion method or by the electrocrystallization technique (CINP) were unsuccessful. So far, the use of CINP leads to easy reprecipitation of the Sn nonoxidized sandwich. Too small crystals unsuitable for crystallographic analysis are obtained in dichlorobenzene.

Reaction of Pc_2TiI_2 and Its Sn Analogue with NaBH_4 . The solid oxidized species, either the Ti or the Sn derivative (50 mg), was suspended in tetrahydrofuran (THF, 3 mL) in the presence of an excess of NaBH_4 . After $1/2 \text{ h}$, the suspension was filtered, and the isolated solid was washed abundantly with methanol and dried under vacuum. The solids were unequivocally identified as Pc_2Ti and Pc_2Sn by their IR spectra. Similar results were obtained with the nitrates and hexafluorophosphates dealt with here (see below).

$[\text{Pc}_2\text{Ti}]\text{NO}_3$. This complex was prepared as already described.¹²

$[\text{Pc}_2\text{Sn}]\text{NO}_3$. The procedure for the preparation of this complex is similar to that used for the corresponding Ti complex: Pc_2Sn -CINP (330 mg) was suspended in HNO_3 (10%) (10 mL), and the suspension was stirred at room temperature for 24 h. After filtration, the solid material was repeatedly washed with water and then with anhydrous ethanol and dried under vacuum (305 mg, yield 85%). Anal. Calcd for $[\text{Pc}_2\text{Sn}]\text{NO}_3$, $\text{C}_{64}\text{H}_{32}\text{N}_{17}\text{O}_3\text{Sn}$: C, 63.77; H, 2.65; N, 19.75. Found: C, 63.10; H, 2.70; N, 18.73.

$[\text{Pc}_2\text{Ti}]\text{PF}_6$ and $[\text{Pc}_2\text{Sn}]\text{PF}_6$. These complexes were obtained from the corresponding nitrates in absolute ethanol (99.7–100%) in the presence of a large excess of the hexafluorophosphate anion, dissolved as NH_4PF_6 . After the mixture was stirred at room temperature for a few hours, the solid material was separated from the solution by filtration, washed with ethanol, and dried under vacuum. Disappearance of the IR absorptions of the nitrate group and appearance of a strong absorption of the PF_6^- anion at ca. 800 cm^{-1} established the complete conversion of the nitrates. Anal. Calcd for $[\text{Pc}_2\text{Ti}]\text{PF}_6$, $\text{C}_{64}\text{H}_{32}\text{F}_6\text{N}_{16}\text{PTi}$: C, 63.12; H, 2.60; N, 18.39. Found: C, 63.04; H, 2.7; N, 18.22. Calcd for $[\text{Pc}_2\text{Sn}]\text{PF}_6$, $\text{C}_{64}\text{H}_{32}\text{F}_6\text{N}_{16}\text{PSn}$: C, 59.66; H, 2.48; N, 17.39. Found: C, 58.58; H, 2.61; N, 16.97.

X-ray Crystal Structure Determination of Pc_2TiI_2 . Crystal structure data were collected by MSC, The Woodlands, TX, and used to solve the structure at the University of Parma, Italy. A black prism-shaped crystal having approximate dimensions of $0.13 \times 0.11 \times 0.08 \text{ mm}$, grown as described above, was mounted in a glass capillary. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 18 carefully centered reflections in the range $14.11 < 2\theta < 17.21^\circ$, corresponding to a tetragonal cell.

The data were collected at a temperature of $-160 \pm 1^\circ \text{ C}$ using the ω - 2θ scan technique to a maximum 2θ value of 49.9° . Scans of $(1.31 + 0.30 \tan \theta)^\circ$ were made at a speed of $8.0^\circ/\text{min}$ (in ω). The weak reflections [$I < 20.0\sigma(I)$] were rescanned (maximum of three rescans), and the counts were accumulated to ensure good counting statistics. Stationary-background counts were recorded on each side of the reflection. A total of 684 reflections were collected. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction, based on azimuthal scans of several reflections,²² resulted in transmission factors ranging from 0.94 to 1.00. The hkl octant

- (19) Silver, J.; Lukes, P. J.; Hey, P. K.; O'Connor, J. M. *Polyhedron* **1989**, *8*, 1631 and references therein.
 (20) Besbes, S.; Plichon, V.; Simon, J.; Vaxiviere, J. J. *Electroanal. Chem. Interfacial Electrochem.* **1987**, *237*, 61 and references therein.
 (21) (a) Maitrot, M.; Guillaud, G.; Boudjema, B.; André, J. J.; Sirzelecka, H.; Simon, J.; Even, R. *Chem. Phys. Lett.* **1987**, *133*, 59. (b) Turek, P.; Petit, P.; André, J. J.; Simon, J.; Even, R.; Boudjema, B.; Guillaud, G.; Maitrot, M. *J. Am. Chem. Soc.* **1987**, *109*, 5119. (c) Belarbi, Z.; Maitrot, M.; Ohta, K.; Simon, J.; André, J. J.; Petit, P. *Chem. Phys. Lett.* **1988**, *143*, 400. (d) Belarbi, Z.; Sirlin, C.; Simon, J.; André, J. J. *J. Phys. Chem.* **1989**, *93*, 8105. (e) Bouvet, M.; Simon, J. *Chem. Phys. Lett.* **1990**, *172*, 299. (f) Liu, Y.; Shigehara, K.; Hara, M.; Yamada, A. *J. Am. Chem. Soc.* **1991**, *113*, 440.

- (22) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Struct. Crystallogr. Chem.* **1968**, *A24*, 351.

was collected, the agreement index between independent equivalent reflections being 0.03.

The coordinates for Ti and I were obtained from a Patterson map. Both atoms lie on 422 sites at (0, 0, 1/4) and (1/2, 1/2, 1/4), respectively, and this requires the titanium atom to be statistically distributed over two positions related by the mirror plane. The subsequent ΔF map showed the Pc molecule to lie on the mirror plane at $z = 0$. Successive refinement, first isotropic and then anisotropic, indicated a positional disorder also for the Pc molecule, most of the atoms [in particular N(1), C(5), and C(6); Figure 5] having abnormally high values for their U_{33} thermal parameters. The Pc molecule was therefore considered to be statistically distributed about the mirror plane and isotropically refined with free coordinates. Only Ti and I were allowed to vary anisotropically. Refinement converged to $R = 0.047$ ($R_w = 0.037$) for 414 observed reflections [$I > 2\sigma(I)$]. All the H atoms were located from a difference map and introduced as fixed contributors ($U_{iso} = 0.03 \text{ \AA}^2$) in the last stage of refinement. The final difference map showed a general background of about 0.3 e \AA^{-3} with a residual electron density of 0.6 e \AA^{-3} spread around the $4/m$ site, i.e. nearly in the center of the Pc molecule. The maximum hole was of $\approx 0.9 \text{ e \AA}^{-3}$. Scattering factors for neutral atoms were taken from ref 23 for non-hydrogen atoms and from ref 24 for H. Among the low-angle reflections, no correction for secondary extinction was deemed necessary. All calculations were carried out on an IBM-AT personal computer equipped with an INMOS T800 transputer using SHELX-76.²⁵

Other Physical Measurements. IR spectra were recorded on a Perkin-Elmer 983 instrument by using Nujol mulls and CsI windows, or KBr pellets. Visible reflectance spectra were obtained on a Cary 2300, by using Halon (PTFE) as reference. Resonance Raman spectra were recorded on a Spex Triplemate Model 1877 spectrograph equipped with a cooled EG & G PARC 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. X-ray powder spectra were recorded on a Seifert 3000 instrument with a Cu $K\alpha$ radiation. EPR data were collected on a Varian V4502-4 spectrometer (X-band). Thermogravimetric analyses were performed on a Du Pont 950 instrument under a N_2 stream (0.5 L/min). Room-temperature dc electrical conductivity measurements were obtained by the Van der Pauw method on the undoped and doped materials at room temperature by using powder pellets pressed at ca. $1.0 \times 10^6 \text{ kPa}$. Elemental analyses for C, H, N, and I (determined potentiometrically) were performed by the Servizio di Microanalisi, Area della Ricerca, CNR (Montelibretti).

Results and Discussion

(A) Pc_2M [$M = Ti(IV), Zr(IV), Sn(IV)$]. Pc_2Ti and Pc_2Sn , the latter prepared by us as the β form³ and both described as cocrystallizing with one molecule of C1NP,^{3,12} were used as starting materials for the oxidation reactions with I_2 and HNO_3 . We observed that occasionally the tin complex contained amounts of C1NP lower than that expected for the 1:1 Pc_2Sn :C1NP molar ratio. If necessary, elimination of solvent from the adducts was normally achieved by heating the samples at 200°C under vacuum (10^{-2} mmHg) for 2 h. No dependence of the nature of the oxidized materials formed on the amount of C1NP contained in the starting Ti or Sn bis(phthalocyanine) complex was observed. The structure of the polymorph α - Pc_2Sn , which can be obtained from the corresponding β form by recrystallization from naphthalene,³ has been elucidated by X-ray analysis.⁵

A brief summary of the structural features of Pc_2Ti ,¹² α - Pc_2Sn ,⁵ and the recently reported Pc_2Zr ¹³ is necessary for further discussion below. Some crystal data of these sandwich-type molecules are given in Table I. In these complexes, as also in other metal bis(phthalocyanines) and metal bis(porphyrins), X-ray work has established^{4,6,7,9,11} that the central metal is eight-coordinated, the surrounding inner N atoms being arranged in the form of a square antiprism. It should be preliminarily noted

Table I. Crystal Data for Bis(phthalocyanine) Complexes

complex	M-N (\AA) ^a	dist between N_4 planes (\AA) ^b	rel rotation (deg) ^c	ref
Pc_2Ti	2.22	2.32	45	12
Pc_2Zr	2.30	2.52 ^d	42	13
Pc_2Sn	2.35	2.70	42	5
$[Pc_2Ti]^{0.66+}$	2.246(7)	2.42	41.1	this work

^a Average M-N distance around the metal atom. ^b Distance between the centroids of the two inner N_4 systems. ^c Staggering angle between two adjacent phthalocyanine rings. ^d This distance was given as 2.20 \AA in ref 13 (see Results and Discussion).

that, among the sandwich-type molecules known, Pc_2Ti ¹² (Figure 1) is a unique species, in which the two macrocyclic ligands are "stapled" together by two inter-ring C-C σ bonds. This results in (a) sp^3 hybridization of the C atoms [C(11), C(11)', C(31), C(31)'; Figure 1] bridging the two macrocycles, with a consequent breaking of the extensive π -electron delocalization present in the "normal" phthalocyanine skeleton, and (b) the closest observed approach of the two inner N_4 - N_4 planes (2.32 \AA , Table I), with very short Ti-N bond distances (2.22 \AA). These peculiar structural features [especially (a)] are responsible for the yellow-orange color of the crystalline complex, which shows, accordingly, typical reflectance and solution (C1NP) visible spectra, with complete absence of absorptions in the Q-band region (550 – 800 nm), usually observed, instead, for "normal" phthalocyanine blue-green materials; the IR spectrum of Pc_2Ti is also quite peculiar.¹²

As shown by X-ray work,¹³ there are no inter-ring C-C σ bonds in Pc_2Zr . Thus, the reported interplanar N_4 - N_4 distance of 2.20 \AA , even shorter than that found in Pc_2Ti , is surprising. The procedure used for the calculation of the N_4 - N_4 distance in Pc_2Zr ¹³ is not clear. By using the normal procedure in determining the positional parameters reported in Table I of ref 13, we obtained a value of 2.52 \AA (Table I) for the centroid-to-centroid separation of the nearly parallel N_4 - N_4 planes (deviation 0.4° between the normals). This distance fits well with the reported corresponding distance (2.53 \AA) "calculated using a simple geometric model"¹³ and seems more reasonable if compared with the data, calculated with the same procedure, for the Ti and Sn complexes. As might be expected, the observed Zr-N distance (2.30 \AA) is slightly longer than that found in Pc_2Ti , also because Zr(IV) has an ionic radius of 0.79 \AA , i.e. 0.11 \AA longer than that of Ti(IV) (0.68 \AA).²⁶ In Pc_2Sn , although the ionic radius of Sn(IV) is only slightly longer (0.71 \AA) than that of Ti(IV), formation of inter-ring C-C σ bonds was not observed.⁵ The separation between the two inner N_4 planes is definitely larger (2.70 \AA), with longer Sn-N bond distances (Table I).

Worthy of note here also is the distortion produced by the attraction of the central metal ion on the Pc rings and, in turn, on the entire bis(phthalocyanine) molecule. This distortion, which is responsible in all cases for the back-to-back facing of the saucer-shaped macrocyclic rings, can be estimated, for instance, by considering the shortest distances of the couples of the outermost carbon atoms of the Pc macrocycle [C(25)-C(24), C(34)-C(35), C(15)-C(14), C(4)-C(5); Figure 1] from the respective inner N_4 plane. Pertinent data for Pc_2Ti and other analogues are given in Table II. It clearly appears that distortion is the greatest in Pc_2Ti , with at least two benzene rings greatly pushed outward, and the least in Pc_2Sn , with that in Pc_2Zr located between. The distortion from planarity in Pc_2Ti is significantly affected by the twisting of the phenyl rings. Such an effect can be evaluated by considering the difference in the distance of each one of the two outermost C atoms of each phenyl ring again from the respective N_4 plane. It can be seen (Table II) that the twisting is most significant for the couples which are in the proximity of the C atoms bridging the two Pc rings [C(34)-C(35), C(15)-C(14); Figure 1].

(23) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 9.

(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) Sheldrick, G. M.; SHELX-76 System of Crystallographic Computer Programs. University of Cambridge, 1976.

(26) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B* **1969**, *25*, 925.

Table II. Distances of the Two Outermost C Atoms of Each Phenyl Ring in the Pc Macrocycle from the Plane of the Relative Inner N₄ System in the Metal Bis(phthalocyanines)

complex	C–N ₄ centroid dist (Å)		ref
	shorter	longer	
Pc ₂ Ti ^a	1.78 (C(25))	1.94 (C(24))	12
	1.10 (C(14))	1.47 (C(15))	
	1.59 (C(5))	1.71 (C(4))	
	1.06 (C(34))	1.52 (C(35))	
Pc ₂ Zr ^b	1.47	1.47	13
Pc ₂ Sn ^b	1.09	1.09	5
[Pc ₂ Ti] ^{0.66+} ^c	0.61 (C(5))	0.67 (C(4))	this work

^a Atom labeling in Figure 1. ^b Due to the symmetry of the molecule, the outermost C atoms of the benzene rings are all equally distant from the N₄ plane. ^c Atom labeling in Figure 5.

Table III. Crystallographic Data for the X-ray Diffraction Studies on Crystalline Pc₂TiI₂

chem formula: C ₆₄ H ₃₂ I ₂ N ₁₆ Ti	space group: <i>P4/mcc</i>
<i>a</i> = 13.841(3) Å	<i>t</i> = -160 °C
<i>b</i> = 13.841(3) Å	<i>λ</i> = 0.710 69 Å
<i>c</i> = 6.370(3) Å	<i>ρ</i> _{calc} = 1.805 g cm ⁻³
<i>α</i> = 90°	<i>μ</i> = 14.88 cm ⁻¹
<i>β</i> = 90°	transm coeff: 0.940–1.000
<i>γ</i> = 90°	<i>R</i> ^a = 0.047
<i>V</i> = 1220.3(7) Å ³	<i>R</i> _w ^b = 0.037
<i>Z</i> = 1	

^a *R* = Σ|Δ*F*|/Σ|*F*_o|. ^b *R*_w = [Σ*w*^{1/2}|Δ*F*|/Σ*w*^{1/2}|*F*_o|].

Table IV. Fractional Atomic Coordinates (×10⁴) for Pc₂TiI₂

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	SOF ^a
Ti(1)	0(-)	0(-)	2500(-)	0.0625
I(1)	5000(-)	5000(-)	2500(-)	0.1250
N(1)	566(4)	1244(5)	598(12)	0.5
N(2)	-843(4)	2277(4)	237(24)	0.5
C(1)	94(7)	2117(5)	281(21)	0.5
C(2)	780(5)	2908(5)	96(66)	0.5
C(3)	664(5)	3885(5)	-330(25)	0.5
C(4)	1509(6)	4451(5)	-455(20)	0.5
C(5)	2409(6)	4025(6)	-356(25)	0.5
C(6)	2524(5)	3052(5)	-129(74)	0.5
C(7)	1690(5)	2488(5)	53(109)	0.5
C(8)	1551(6)	1451(6)	311(18)	0.5

^a SOF = site occupation factor.

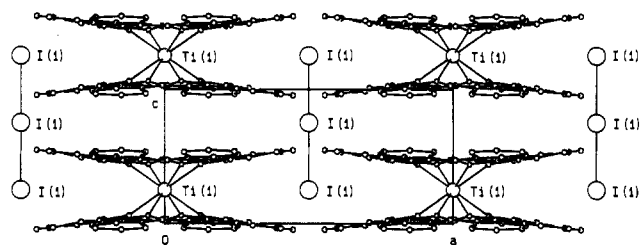
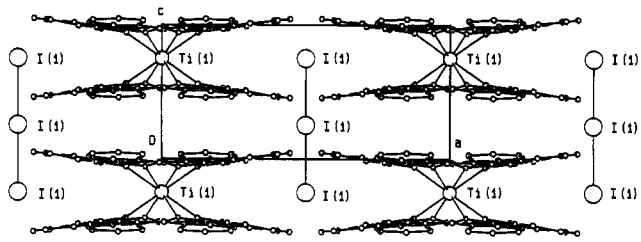
(B) Pc₂M₂ [M = Ti(IV), Sn(IV)]. (i) General Properties. Pc₂TiI₂ and its Sn(IV) analogue, greenish-black, stable to air, microcrystalline materials, are easily obtained by oxidation of their corresponding precursors Pc₂M [M = Ti(IV), Sn(IV)] with excess I₂. There is apparently no dependence of the formation of the doped species on the amount of I₂ used. Even in the presence of scarce amounts of I₂, for instance by using a Pc₂Ti:I₂ ratio of 1:1/2, the Ti derivative formed does not change its composition and some unreacted Pc₂Ti is eventually recovered from the reaction. This behavior indicates a high tendency of the reaction to form Pc₂TiI₂, as has been found also for Pc₂SnI₂. Thermogravimetric analysis shows that both Pc₂TiI₂ and Pc₂SnI₂ are stable in the range 25–100 °C. At higher temperatures weight loss is observed, probably due to some elimination of iodine. However, in no case was the initial bis(phthalocyanine) complex exclusively reobtained as a pure material, the loss of iodine being very likely concomitant with some decomposition of the oxidized material used; no detailed study was made of the materials formed as a function of temperature.

It is relevant that the reaction of Pc₂TiI₂ and Pc₂SnI₂ with NaBH₄ results reproducibly in their total conversion into the original precursors, as was already anticipated for [Pc₂Ti]NO₃.¹² This forward and reverse redox process undergone by Pc₂Ti and Pc₂Sn is important, particularly in the case of Pc₂Ti, in view of the associated structural changes implied (see below).

Table V. Bond Distances (Å) and Angles (deg) for Pc₂TiI₂^a

Ti(1)–N(1)	2.246(7)	C(2)–C(3)	1.388(13)
N(1)–C(1)	1.388(10)	C(2)–C(7)	1.387(10)
N(1)–C(8)	1.405(10)	C(3)–C(4)	1.410(11)
N(2)–C(1)	1.316(11)	C(4)–C(5)	1.380(12)
N(2)–C(8)	1.311(10)	C(5)–C(6)	1.364(12)
C(1)–C(2)	1.454(11)	C(6)–C(7)	1.398(12)
C(7)–C(8)	1.457(13)		
N(1)–Ti(1)–N(1)′	73.1(2)	C(2)–C(3)–C(4)	117.1(7)
N(1)–Ti(1)–N(1)″	75.9(2)	C(3)–C(4)–C(5)	120.6(7)
Ti(1)–N(1)–C(8)	124.4(5)	C(4)–C(5)–C(6)	122.2(7)
Ti(1)–N(1)–C(1)	125.5(6)	C(5)–C(6)–C(7)	117.6(7)
C(1)–N(1)–C(8)	105.1(7)	C(2)–C(7)–C(6)	121.1(6)
N(1)–C(1)–N(2)	127.8(6)	C(6)–C(7)–C(8)	131.9(7)
N(2)–C(1)–C(2)	121.0(7)	C(2)–C(7)–C(8)	106.9(6)
N(1)–C(1)–C(2)	111.1(7)	N(2)′–C(8)–C(7)	121.8(7)
C(1)–C(2)–C(7)	106.2(6)	N(1)–C(8)–C(7)	110.1(7)
C(1)–C(2)–C(3)	132.3(7)	N(1)–C(8)–N(2)′	128.1(7)
C(3)–C(2)–C(7)	120.6(7)		

^a Single prime = *y*, -*x*, *z*. Double prime = -*x*, *y*, 1/2 - *z*.

**Figure 2.** Crystal structure of Pc₂TiI₂ viewed perpendicular to the macrocycle stacking direction, as present in 50% of the unit cells.**Figure 3.** Crystal structure of Pc₂TiI₂ viewed perpendicular to the macrocycle stacking direction, as present in the other 50% of the unit cells.

(ii) X-ray Crystal Structure of Pc₂TiI₂. Crystal data and fractional atomic coordinates for Pc₂TiI₂ are given in Tables III and IV, respectively, and bond distances and angles are summarized in Table V.

The structure consists of columnar stacks of positively charged [Pc₂Ti]^{0.66+} units, well separated from linearly elongated chains of I₃⁻ ions. Both these charged monodimensional aggregates are aligned along the *c* axis of the crystal (Figures 2–4). The crystallographically imposed 4/*m* symmetry requires a statistical distribution of the complex molecules; thus, the structure can be considered as consisting of ordered columnar stacks of metal bis(phthalocyanine) units, disordered with respect to neighboring stacks. In particular, the structure shown in Figure 2 should be present in 50% of the unit cells, the residual 50% having a centrosymmetric structure (Figure 3). The 4/*m* symmetry is therefore the result of crystal packing. This model was satisfactorily refined (see Experimental Section).

The presence of chains of disordered I₃⁻ ions recalls the comparable situation found in the structure of NiPcI.^{1a} Moreover, although the Pc:M ratios are different for the two species, Pc₂TiI₂ and PcNiI have the same space group, *Pa/mcc*, and practically identical cell dimensions; thus, they are isostructurally arranged in the crystal. The average distance of adjacent Pc rings along the stacking axis in Pc₂TiI₂ is 3.19 Å, shorter than any other found in the several similar phthalocyanine-doped aggregates (3.22–3.25 Å; see ref 1e and references therein), which

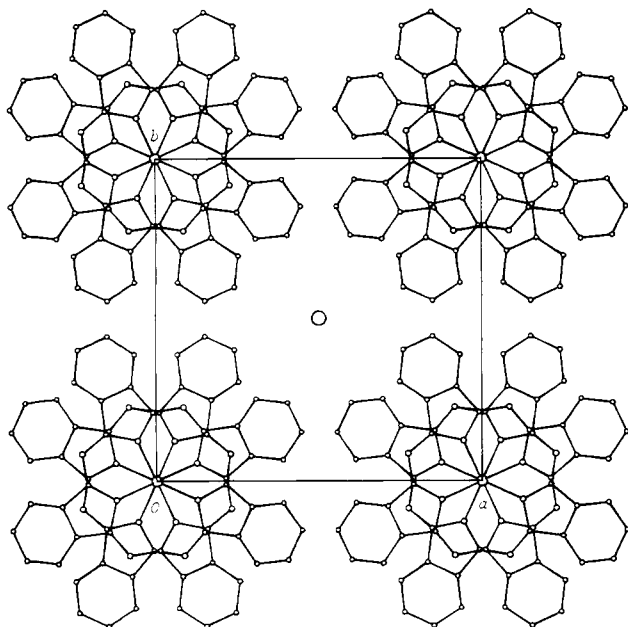


Figure 4. Crystal structure of Pc_2TiI_2 viewed parallel to the macrocycle stacking direction.

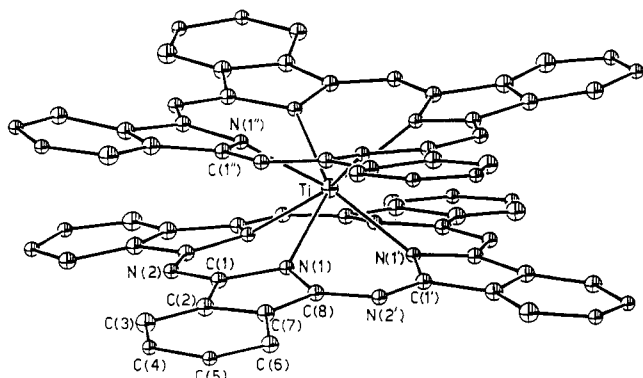


Figure 5. ORTEP view (50% probability ellipsoids) of the $[\text{Pc}_2\text{Ti}]^{0.66+}$ cation showing the labeling scheme adopted. Prime and double prime signs refers to transformations of $-y, x, z$ and $y, x, 1/2 - z$, respectively.

show good electrical conductivity properties. The positive charge (0.66+) assigned to the Pc_2Ti moiety is directly derived from the stoichiometry of the complex. An ORTEP drawing of the $[\text{Pc}_2\text{Ti}]^{0.66+}$ unit with the atom labeling is given in Figure 5. As in its precursor Pc_2Ti , the titanium atom is sandwiched between the two staggered (41.1°) Pc rings and is surrounded by the eight nitrogen atoms of the two inner N_4 systems, forming the usual square antiprism around the central metal.

The most important observation is that in $[\text{Pc}_2\text{Ti}]^{0.66+}$ the inter-ring C-C σ bonds, found in Pc_2Ti , are no longer present. The new distance C(1)–C(1') [following the numbering designation in Figure 5; C(11)–C(11'), 1.556(6) Å, and C(31)–C(31'), 1.575(6) Å, in Figure 1] is now much longer, i.e. 2.839(19) Å. Thus, there is an effective breaking of the inter-ring σ bonds consequent to the doping process, followed by the reinsertion of each C(1) carbon atom into the framework of the respective Pc ligand. This, in turn, results in a marked release of strain within the sandwiched molecule, with an implied reinforcement of the original delocalization of the π -bond system in each one of the two Pc rings. The latter effect is clearly evidenced by accurately comparing the C–C and C–N bond distances present in $\text{Pc}_2\text{Ti}^{12}$ and in $[\text{Pc}_2\text{Ti}]^{0.66+}$ (Figure 5 and Table V). Nevertheless, the two Pc rings in $[\text{Pc}_2\text{Ti}]^{0.66+}$ are still far from approaching planarity, as indicated by the following data:

(a) The two inner N_4 systems, which, due to symmetry requirements, are perfectly planar and parallel to one another,

Table VI. X-ray Powder Data for Pc_2TiI_2 and Pc_2SnI_2 : d (Å)

Pc_2TiI_2	Pc_2SnI_2	Pc_2TiI_2	Pc_2SnI_2
13.97 w	13.90 s	3.28 vw	3.29 w
9.83 vs	9.84 vs	3.23 vs	3.22 w
6.96 w	6.97 s	3.14 vs	3.12 m
6.22 s	6.22 s	3.07 s	3.05 w
6.12 m		2.93 s	2.92 m
5.20 vw		2.73 vw	2.73 m
4.92 vw	4.92 m	2.70 m	2.69 w
4.63 m	4.64 w	2.60 m	2.60 w
4.48 s	4.47 s	2.36 vw	
4.40 m	4.40 s	2.24 vw	2.24 vw
3.86 m	3.86 w	1.89 vw	2.20 vw
3.37 w	3.48 w	1.62 vw	1.97 vw

are located 2.42 Å apart (Table I), i.e. at a distance which is only 0.1 Å longer than that in Pc_2Ti , and are shorter than any other corresponding distance in similar undoped sandwiched molecules; incidentally, distances to be also noted are Ti–C_i, 1.21 Å (C_i = center of the N_4 plane), and Ti–N(1), 2.246(7) Å, the latter a little longer than the corresponding average distance, 2.22 Å, in Pc_2Ti .

(b) The Pc rings, as a whole, are certainly more flattened than in Pc_2Ti , as can be seen by considering the maximum distances of the outermost C atoms of the phenyl rings from the respective inner N_4 plane, with respect to those found in Pc_2Ti (Table II). Noticeably, however, the furthest C atom is still 0.67 Å away from the N_4 plane. It appears that the contribution to distortion from planarity by the twisting of the phenyl rings, consistent in Pc_2Ti , is substantially reduced in $[\text{Pc}_2\text{Ti}]^{0.66+}$.

Due again to symmetry requirements, the geometries (bond distances and angles) of the four isoindole groups of each Pc moiety in $[\text{Pc}_2\text{Ti}]^{0.66+}$ are identical, and the two Pc rings are also undistinguishable. This means that the positive charge of the π radical bis(phthalocyanine) unit is equally shared by the two Pc residues.

From the previous¹² and the above X-ray data it is unequivocally established that the oxidation process which converts Pc_2Ti to Pc_2TiI_2 , the reverse process with NaBH_4 , and the parallel forward and backward processes involving the formation of $[\text{Pc}_2\text{Ti}]\text{NO}_3$ and $[\text{Pc}_2\text{Ti}]\text{PF}_6$ (see below) imply respectively the breaking and repair of the inter-ring C–C σ bonds. However, as we discussed previously,¹² this peculiar structural "breathing" of the Pc_2Ti sandwiched entity is not intrinsically a redox process, rather an accompanying process. The redox process, instead, which is common to both the Ti and Sn complexes, is responsible for the construction and disruption of the monodimensional aggregate shown by X-ray analysis for Pc_2TiI_2 .

(iii) X-ray Powder, IR, and Raman Spectra of Pc_2TiI_2 and Pc_2SnI_2 . The structural similarity of Pc_2SnI_2 to Pc_2TiI_2 , suggested by elemental analysis and thermogravimetric and redox behavior, is further supported by X-ray powder, IR, and resonance Raman spectra.

A very important structural relationship between Pc_2TiI_2 and Pc_2SnI_2 is illustrated by their X-ray powder spectra (Table VI). These spectra show practically identical positions and numbers of lines. Despite some inconsistencies as to the intensity of corresponding lines, the two spectra are taken as indicative of practically isostructural crystalline materials. Thus, a large part of the crystallographic information available on the Ti compound can be transferred to its Sn analogue.

The IR spectra of the two complexes in the region 4000–450 cm^{-1} (Figure 6) are almost identical. They both show features typical of highly electrically conducting phthalocyanine systems: (a) a broad exciton absorption occupying a large part of the region explored; (b) the associated low intensity of the IR absorptions of the Pc ring. The only difference between the two spectra worth mentioning is the presence of two weak absorptions in the region 1550–1500 cm^{-1} in the spectrum of the Ti complex (arrows), which are not observed for the Sn complex. These two

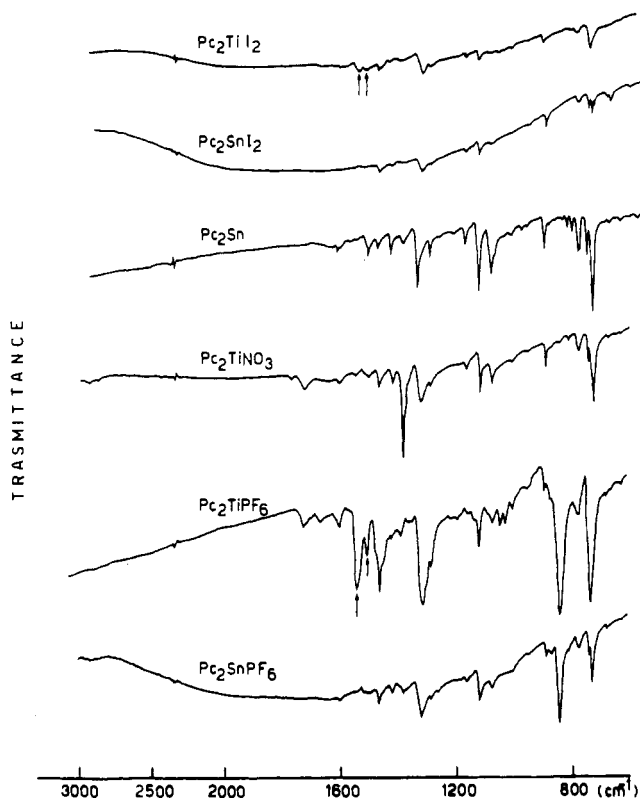


Figure 6. IR spectra (KBr) of various Ti and Sn species. Arrows in the region 1550–1500 cm^{-1} indicate absorptions which appear to be typical of the Ti complexes (see Results and Discussion).

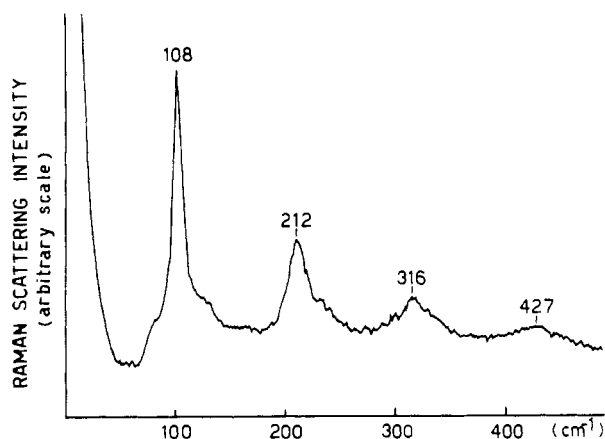


Figure 7. Resonance Raman spectrum of Pc_2SnI_2 .

bands are specific for the Ti complexes, having been observed (more easily detectable) for Pc_2Ti and $[\text{Pc}_2\text{Ti}]\text{NO}_3$ ¹² and also for $[\text{Pc}_2\text{Ti}]\text{PF}_6$ (Figure 6). Significantly, in spite of the low intensity of the ring absorptions, the two spectra clearly resemble more closely that of Pc_2Sn (Figure 5), in which “normal” phthalocyanine ring absorptions are present, rather than that of the “stapled” Pc_2Ti .¹²

The resonance Raman spectra of both Pc_2TiI_2 and Pc_2SnI_2 show the presence of an intense narrow band at 108 cm^{-1} , with overtones at 212–214, 316–320, and ca. 427 cm^{-1} (see Figure 7 for Pc_2SnI_2). This band system is unequivocally indicative of the presence of I_3^- ions in the crystal structure of these compounds. There is no evidence in the spectrum of the presence of alternative iodine aggregates (I_5^- , $\approx 160 \text{ cm}^{-1}$; I_2 , $\approx 200 \text{ cm}^{-1}$; I_2 coordinated to I_3^- , $\approx 180 \text{ cm}^{-1}$), as is also the case for the spectrum of Pc_2TiI_2 . These data confirm the presence of I_3^- ions in these complexes and, in keeping with their stoichiometry and the X-ray work on Pc_2TiI_2 , the formulation already given, i.e. $[\text{Pc}_2\text{M}](\text{I}_3)_{0.66}$ [$\text{M} =$

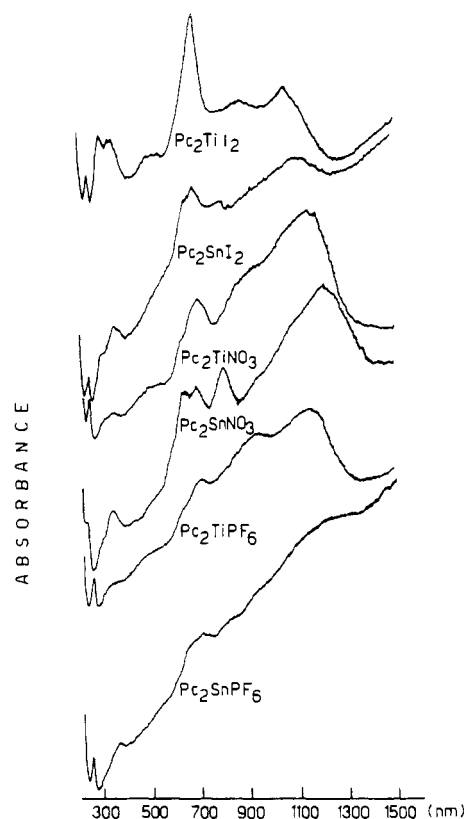


Figure 8. Reflectance spectra of the oxidized species in the visible-near-IR region.

Ti(IV), Sn(IV)], with the $[\text{Pc}_2\text{M}]$ moiety carrying the positive charge of 0.66+, as the correct one.

It is relevant to observe that the positive charge of the cationic bis(phthalocyanine) moiety $[\text{Pc}_2\text{M}]^{0.66+}$ is necessarily ligand centered, since further oxidation for either Ti(IV) or Sn(IV) is not possible. The formation of the π radical cation is also supported by reflectance and EPR spectra (see below).

(C) $[\text{Pc}_2\text{M}]\text{NO}_3$ and $[\text{Pc}_2\text{M}]\text{PF}_6$ [$\text{M} = \text{Ti(IV), Sn(IV)}$]. These oxidized species are all stable to air. Since they are essentially amorphous materials, no structural information is available on these complexes from X-ray powder spectra. Their stoichiometry indicates an integrally monopositively charged unit $[\text{Pc}_2\text{M}]^+$. The IR spectra of the nitrates (ref 12 for Ti; Figure 6 for Sn) are characterized by an intense absorption located at 1383 cm^{-1} for both complexes assigned to noncoordinated NO_3^- . Weakening of the Pc absorptions, as expected for doped materials, is more evident in the spectrum of $[\text{Pc}_2\text{Sn}]\text{NO}_3$ (taking the intensity of the band at 1383 cm^{-1} as reference). No “metallic” bands are observed. The two PF_6^- derivatives show the typical intense absorption of this anion located at 841–842 cm^{-1} (Figure 6). The Sn complex shows clearly the broad metallic band and the accompanying weakening of the Pc absorptions. The Ti complex shows the two moderately intense absorptions, located at 1507 and 1544 cm^{-1} , previously dealt with, which appear reminiscent of the corresponding very intense absorptions observed in the same position in the IR spectrum of Pc_2Ti .

(D) **Reflectance and EPR Spectra and Electrical Conductivity Data for All the Oxidized Species.** The reflectance spectra of all the present complexes (Figure 8) show essentially similar features, with absorptions in the near-UV, visible, and near-IR regions. The occurrence in all the spectra of more or less detectable absorptions around 700 nm indicates that the phthalocyanine chromophore is essentially “normal”, which means that, for the nitrate and hexafluorophosphate complexes, as for Pc_2TiI_2 , oxidation has produced the breaking of the interligand C–C bonds present in Pc_2Ti , in keeping with X-ray information and IR spectral data. A weak absorption band at about 500 nm, often qualified

Table VII. EPR and Conductivity Data

	EPR			σ ($\Omega^{-1} \text{ cm}^{-1}$) ^c
	T^a	g	H (G) ^b	
Pc ₂ Ti				<10 ⁻⁹
Pc ₂ TiI ₂	RT	2.0020	6.1	(0.5–5.0) × 10 ⁻³
[Pc ₂ Ti]NO ₃	LN	2.0014	2.5	ca. 10 ⁻⁵
	RT	2.0011	2.8	
[Pc ₂ Ti]PF ₆	LN	2.0016	2.0	ca. 5 × 10 ⁻⁴
	RT	2.0012	3.1	
Pc ₂ Sn				ca. 10 ⁻⁸
Pc ₂ SnI ₂	LN	2.0027	5.0	(0.5–5.0) × 10 ⁻²
[Pc ₂ Sn]NO ₃	RT	2.002	1.0	ca. 5 × 10 ⁻⁴
	LN	2.0019	1.0	
[Pc ₂ Sn]PF ₆	RT	2.002	1.1	ca. 10 ⁻⁴

^a RT = room temperature; LN = liquid-nitrogen temperature. ^b Signal width. ^c Average values from measurements at room temperature on several powdered polycrystalline samples. Normally, no variation was observed if measurements were taken on the same sample after several months.

as typical of π radical cationic phthalocyanine species,^{8,27,28} is detectable in all the spectra reported. The near-IR region (900–1300 nm) is dominated by broad intense absorptions previously observed for other bis(phthalocyanine) and bis(porphyrin) materials (see ref 16 and references therein) and probably interpretable in terms of intradimer, fractional or unitary, charge transfer, account being taken, for the present complexes, of the occurrence of close interdimer contacts.

The EPR spectra of all the oxidized materials show a single, rather narrow peak in the proximity of the free-electron g value (2.0023). Data are given in Table VII. These data are clearly indicative of the formation of a ligand-centered π cation radical, in keeping with expectation. Since, as discussed before, the two phthalocyanine rings are identical in bond lengths and angles, it is once again noticed here that the ligand-centered oxidation is homogeneously affecting both ligands. There are no examples reported in the literature of similar doped metal bis(phthalocyanines) for comparison with those reported here. We might note that, in the case of [Pc₂Lu^{III}]⁺, in which a formal description would predict the presence of both a Pc(1-)[•] and a Pc(2-) ligand,

- (27) Nyokong, T.; Gasina, Z.; Stillmann, M. *J. Inorg. Chim. Acta* **1986**, *112*, 11.
 (28) Kasuga, K.; Motonori, A.; Morimoto, H. *Inorg. Chim. Acta* **1986**, *112*, 99.

different structural features for the two Pc residues have been observed.⁷ However, no direct relationship has been derived in that case between the radical nature of the sandwich molecule and the different structural arrangements of the two Pc residues.

All the σ (RT) values summarized in Table VII are in the range expected for semiconductors. Pc₂SnI₂ shows conductivity values which are definitely 1 order of magnitude higher than those for Pc₂TiI₂ and which are the highest values among those measured for the species under examination. The Sn nitrate and hexafluorophosphate complexes also show slightly higher values than the corresponding Ti derivatives. It should be noted that the doped species for which the highest values of conductivity are observed, i.e. Pc₂SnI₂, its Ti analogue, and [Pc₂Sn]PF₆, are those which show the broad "metallic" band in the IR spectrum (Figure 6). The higher conductivities shown by the Sn complexes with respect to those of the corresponding Ti complexes is probably related to the structural features of the present materials. We can confidently assume for Pc₂TiI₂ and Pc₂SnI₂ similar stackings of the molecules along the c axis with comparable average interring distances. If this is true, then, when considering that in going from Pc₂Ti to Pc₂TiI₂ the intramolecular distance of the N₄-N₄ planes increases from 2.32 to 2.42 Å, one should expect the same distance to increase from 2.70 Å, as found in Pc₂Sn, to a longer value in Pc₂SnI₂, thus resulting in a closer approach to planarity in the latter than in Pc₂TiI₂. Reasonably, this effect should favor charge transfer through the chain of the [Pc₂Sn]^{0.66+} units, thus justifying the higher electrical conductivity values observed. A similar explanation can be suggested for the couples of nitrates and hexafluorophosphates.

Acknowledgment. The assistance of Dr. G. Mattei (IMAI) in recording the Raman spectra is gratefully acknowledged. Thanks are expressed to F. Dianetti and L. Petrilli (ICMAT) for elemental analyses, to G. Chiozzini (ICMAT) for thermogravimetric analyses, and to C. Veroli (IMAI) for X-ray powder spectra. The authors acknowledge financial support from the Italian Consiglio Nazionale delle Ricerche (CNR) and support for C.E. from MURST (60%).

Supplementary Material Available: Experimental data for the X-ray diffraction study on Pc₂TiI₂ (Table SI) and related listings of fractional atomic coordinates for hydrogen atoms (Table SII) and isotropic and anisotropic thermal parameters (Table SIII) (3 pages). Ordering information is given on any current masthead page.