One Step Forward to “Stapled” Bis(phthalocyanine) Metal Complexes: Synthesis, Characterization, and Redox Properties of Bis(phthalocyaninato)niobium(IV). X-ray Crystal Structure of the Monoelectronically Oxidized Species $[Pc_2Nb](I_3)(I_2)_{0.5}(ClNP)_{3.5}$ (ClNP = 1-Chloronaphthalene)

Maria Pia Donzello,[†] **Claudio Ercolani,***[,†] **Angiola Chiesi-Villa,**[§] **and Corrado Rizzoli**[§]

Dipartimento di Chimica, Università degli Studi di Roma “La Sapienza”, Roma, Italy, and
Istituto di Strutturistica Chimica, Università di Parma, Parma, Italy

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Bis(phthalocyaninato)niobium(IV) has been prepared and isolated as a monosolvate, $[Pc_2Nb]\cdot ClNP$ (ClNP = 1-chloronaphthalene). It is a light-brown, stable-to-air Nb(IV) (d^1) paramagnetic sandwich-like species, which, upon oxidation by I_2 under mild conditions, undergoes a metal-centered monoelectronic oxidation to give the diamagnetic Nb(V) (d^0) $[Pc_2Nb]^+$ fragment, with formation of saltlike species of formula $[Pc_2Nb](I_3)(I_2)0.5(ClNP)_{3.5}$ (**I**). The structure of **I** has been elucidated by single-crystal X-ray work. Crystals are triclinic: formula $C_{64}H_{32}N_{16}Nb\cdot I_3\cdot 0.5I_2\cdot 3.5C_{10}H_7Cl$, $M = 2194.8$, $a = 17.702(3)$ Å, $b = 18.708(3)$ Å, $c = 13.504(2)$ Å, $V = 4267.5(13)$ Å^3, $\alpha = 106.00(2)°$, $\beta = 93.39(2)°$, $\gamma = 83.26(1)°$, $Z = 2$, space group $P\bar{1}$. The structure of the $[Pc_2Nb]^+$ fragment, “stapled” by two inter-ligand C−C σ bonds (C11A−C11B and C31A−C31B = 1.574(15) Å), together with its color and UV−visible spectral behavior, allows a straightforward assignment of the same “stapled” structure to the unoxidized $[Pc_2Nb]$. The present niobium sandwiched materials reiterate the peculiar structural findings shown only by the previously reported $[Pc_2Ti]$.

Introduction

There has been increasing interest in the last ten to fifteen years in the synthesis, investigation of structure, and examination of properties of metal bis(phthalocyanine) complexes, Pc_2M, M being mainly a rare-earth element, owing, prevalently, to the interesting electrochromic properties of the species formed.[1] Among the Pc_2M species reported, including some first-[2] and second-row transition[3,4] and nontransition metal derivatives,[3,5] bis(phthalocyaninato)titanium(IV), Pc_2Ti,[2] has been, until very recently, the unique example reported of a sandwiched material showing the two macrocyclic units “stapled” together by two inter-ligand C−C σ bonds. In Pc_2Zr,[4] although the two phthalocyanine rings are far from planar, no inter-ligand C−C σ bonds have been found present. We have been further exploring the formation of Pc_2M species by using metal centers in the area of the early transition metals and very recently anticipated[6] that Pc_2Nb, obtained by the reaction of $PcNbCl_2$[7] and $PcNa_2$[8] in ClNP, also exhibits an unusual color (light-brown) and IR and UV−visible spectral features closely recalling those of Pc_2Ti, all data taken as unequivocal signals of a “stapled” structure also present in the new Nb(IV) sandwiched species. We report here in more detail on the synthetic procedure for the formation of Pc_2Nb and give more information on its electronic structure and redox properties. Information at hand, also contributed by the elucidation of the structure of the species $[Pc_2Nb](I_3)(I_2)_{0.5}(ClNP)_{3.5}$, indicates that monoelectronic oxidation of Pc_2Nb is metal centered, a distinct behavior from that shown by Pc_2Ti, and that, after oxidation, the “stapled” structure is retained practically unchanged.

Experimental Section

$PcNbCl_2$[7] and $PcNa_2$[8] were prepared by literature methods.

$[Pc_2Nb]\cdot$ClNP. The complex was obtained from $PcNbCl_2$ and $PcNa_2$ in ClNP with the following exemplified procedure.

Solid $PcNbCl_2$ (2.90 g, 4.29 mmol) and $PcNa_2$ (2.88 g, 5.15 mmol) (molar ratio 1:1.2) are heated at 120 °C under vacuum (10^{-2} mmHg) for 80 min in a 100 mL flask. Freshly distilled ClNP (50 mL) is then added, and the mixture is heated under nitrogen at 220 °C for 4 h, with stirring. A considerable amount of solid (>4 g; mostly PcH_2, plus NaCl) is separated from the hot reaction mixture by centrifugation. Soon after cooling, centrifugation is repeated twice in about 1 h with separation of a smaller amount of material (100−200 mg, mostly PcH_2). The solution is then kept in the refrigerator overnight, and the solid precipitated is separated, washed with *n*-hexane repeatedly, and brought to constant weight under vacuum (437 mg, portion I). Addition of *n*-pentane (40 mL) to the mother liquors, followed by cooling of the mixture in the refrigerator for 12 h, causes further precipitation of material, which is washed with *n*-hexane and brought to constant weight under vacuum (674 mg, portion II). Both portions need purification by crystallization from boiling ClNP, providing ca. 700 mg of clean light-brown microcrystalline material corresponding to the formula [Pc2-

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* Corresponding author. E-mail: ercolani@axrma.uniroma1.it.

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[§] University of Parma.

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Nb]·ClNP (overall yield: ca. 13−14%). Calcd for $C_{74}H_{39}ClN_{16}Nb$: C, 69.41; H, 3.07; N, 17.50. Found: C, 69.23; H, 3.27; N, 17.44.

$[Pc_2Nb](I_3)(I_2)_{0.5}(ClNP)_{3.5}$ (I). $[Pc_2Nb]$·ClNP (200 mg, 0.10 mmol) and bisublimed I_2 (1.06 g, 4.16 mmol) (molar ratio 1:26) are suspended in anhydrous benzene, and the mixture is stirred under nitrogen at room temperature for 72 h. The ground solid is separated from the solution by centrifugation, washed repeatedly with benzene and acetone, and brought to constant weight under vacuum (236 mg). Complex **I** is obtained in the form of dark-brown prismatic crystals, suitable for single-crystal X-ray examination (see below), when purified by slow recrystallization from hot ClNP (80 °C). Calcd for $C_{99}H_{56.5}Cl_{3.5}I_4N_{16}$-Nb: C, 54.18; H, 2.59; N, 10.21. Found: C, 53.50; H, 2.50; N, 10.29.

Reduction of I with $NaBH_4$. Complex **I** (24 mg) is suspended in benzene (10 mL) together with $NaBH_4$ (52 mg), and the mixture is stirred at room temperature for 19 h. After filtration, the solid isolated is washed with EtOH, H_2O, again with EtOH, and brought to constant weight under vacuum. The IR spectrum of the solid unequivocally indicates that reduction of **I** to the original Pc_2Nb occurred.

X-ray Data for I. A suitable crystal was mounted in a glass capillary and sealed under nitrogen. The reduced cells were obtained with use of TRACER.[9] Data were collected at 295 K on a Philips PW1100 single-crystal diffractometer. For intensities and background the individual reflection profiles were analyzed.[10] The structure amplitudes were obtained after the usual Lorentz and polarization corrections,[11] and the absolute scale was established by the Wilson method.[12] The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected. Data were then corrected for absorption using a semiempirical method.[13] The function minimized during the least-squares refinements was $\Sigma w(\Delta F^2)^2$. Anomalous scattering corrections were included in all structure factor calculations.[14] Scattering factors for neutral atoms were taken from ref 14a for nonhydrogen atoms and from ref 15 for H. Structure solutions were based on the observed reflections [$I > 2\sigma(I)$], while the refinements were based on the unique reflections having $I > 0$. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map.[16] Refinement was done by full-matrix least-squares first isotropically and then anisotropically for all non-H atoms except for the disordered atoms. Troubles were encountered in the refinement of the ClNP solvent molecules of crystallization because of rather high values reached by the U_{ij} parameters of carbon atoms indicating the presence of severe disorder. Attempts to split the carbon atoms in "partial" atoms were unsuccessful. The atoms were then anisotropically refined, constraining the aromatic rings to have a D_{6h} symmetry. Moreover, some relevant residual peaks were found in the proximity of the C51, ..., C60 and C71, ..., C80 aromatic rings, simulating the presence of a statistical distribution between 1- and 2-chloronaphthalene. The best fit was obtained by splitting the Cl2 chlorine atom over four positions, called A, B, C, and D, and the Cl4 chlorine atom over three positions, called A, B, and C. The atoms were isotropically refined with site occupation factors of 0.25 for the four positions of Cl2 and 0.55, 0.25, and 0.20 for the A, B, and C positions, respectively, of Cl4. The Cl3, C71, ..., C75 chloronaphthalene molecule was found to lie about a center of symmetry requiring the statistical distribution over two positions of the chlorine atom, which was then anisotropically refined with a site occupation factor of 0.5.

The hydrogen atoms of the phthalocyanine ligands were put in geometrically calculated positions and introduced in the refinements as fixed atoms contributions ($U_{iso} = 0.10$ Å^2). The H atoms associated to the ClNP solvent molecules were ignored.

In the last stage of refinement the weighting scheme $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ (with $P = (F_o^2 + 2F_c^2)/3$ was applied with a resulting in the value of 0.0972. All calculations were performed with Shelx92.[17] The final difference maps showed no unusual features, with no significant peaks above the general background, except for six residual peaks in the range 1.11−0.84 e Å^{-3} located in the proximity of the iodine atoms.

Other Physical Measurements. IR spectra were run on a Perkin-Elmer 783 spectrophotometer by using Nujol mulls between CsI plates. Room-temperature magnetic susceptibility measurements were carried on a permanent magnet (7000 G), by using the Gouy method and a $NiCl_2$ solution as calibrant. Thermogravimetric analyses were performed on a Stanton Re model STA-781 analyzer in a N_2 atmosphere (0.5 L/min). Elemental analyses for C, H, and N were performed by the Servizio di Microanalisi, Area della Ricerca, CNR (Montelibretti). UV−visible spectra were recorded on a Varian Cary 5E spectrophotometer. Low-temperature (80 K) EPR spectra were obtained on a Varian V 4502-4 spectrometer (X-band) by using the Centre E1′ as marker ($g = 2.0008$). Resonance Raman spectra were recorded on a Spex Triplemate model 1877 spectrograph equipped with a cooled EG&G PARC model 1454 OMA detector. X-ray powder spectra were recorded on a Philips model PW 1710 instrument with Cu Kα radiation.

Results and Discussion

$[Pc_2Nb]$: General Aspects. Pc_2Nb is a light-brown species indefinitely stable in air. It is obtained as a monosolvate from ClNP, i.e., $[Pc_2Nb]$·ClNP. As such, the complex exhibits an X-ray powder spectrum very similar, although not strictly identical, to that of the Ti(IV) analogue $[Pc_2Ti]$·ClNP.[2] Owing to its peculiar color and IR and UV−visible spectral behavior, a "stapled" structure of the type observed for Pc_2Ti was recently suggested.[6] No support could be provided by X-ray work, since attempts of preparation of single crystals of Pc_2Nb in a variety of solvents were all unsuccessful, leading in many attempts only to the formation of single crystals too small for X-ray examination. As it is shown below, however, X-ray work on an oxidized species definitely confirms the structural features already suggested.

The presence of Nb(IV) (d^1) in Pc_2Nb is proved by its paramagnetism ($\mu_{eff} = 1.69\ \mu_B$),[6] and also strongly supported by EPR measurements. Figure 1 shows the experimental low-temperature EPR spectrum (78 K) of Pc_2Nb magnetically diluted into its corresponding diamagnetic matrix, i.e., $[Pc_2Ti]$, and the associated simulated spectrum. The observed hyperfine structure, which is due to the coupling of the unpaired electron with the nuclear spin of Nb(IV) ($I = {}^9/_2$), allows estimation of anisotropic g and A values ($g_{\parallel} = 1.895$; $g_{\perp} = 1.908$; $A_{\parallel} = 194$ G; $A_{\perp} = 171$ G), indicative of an axial symmetry. A similar spectrum is also obtained by a frozen solution (80 K) of the complex in ClNP.

Oxidation of $[Pc_2Nb]$. Pc_2Nb is easily oxidized by iodine, under mild conditions, with formation of the species $[Pc_2Nb](I_3)(I_2)_{0.5}(ClNP)_{3.5}$ (**I**), containing the $[Pc_2Nb]^+$ unit. Clearly, then, the oxidation proceeds differently than for Pc_2Ti, from which, upon oxidation with iodine, the nonintegrally oxidized unit $[Pc_2Ti]^{+0.66}$ is obtained in the species $[Pc_2Ti](I_3)_{0.66}$, a solid electrically conducting material containing linear chains of cations aligned parallel to chains of I_3^- units.[18] In such a case

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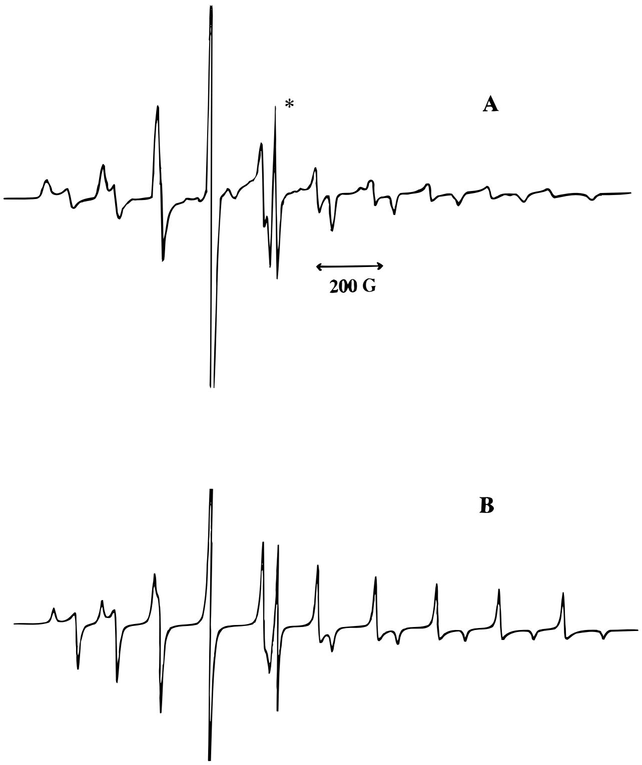

Figure 1. (a) Low-temperature (78 K) EPR spectra of solid Pc_2Nb diluted in Pc_2Ti (A, experimental; B, simulated; the asterisk refers to the Centre E1′ marker, $g_{av} = 2.0008$).

Table 1. UV−Visible Solution Spectra in CH_2Cl_2 of $[Pc_2Nb]$ and Its Oxidized Species

complex	λ, $\epsilon \times 10^4$ (nm, $dm^3\ mol^{-1}\ cm^{-1}$)	
$[Pc_2Nb]$	243, 8.89	298, 7.49
I[a]	253, 11.2	303, 12.3

[a] Very weak shoulders at 335 and 480 nm.

the oxidation could be exclusively ligand centered, owing to the presence of the inoxidizable Ti(IV) (d^0). In Pc_2Nb, a metal-centered monoelectronic oxidation Nb(IV) → Nb(V) is an effective alternative possibility, *which, indeed, does take place*. This is supported by the combined information from magnetic and EPR data, color of the material, UV−visible spectral data, and, ultimately, by X-ray work on the species **I** (see below). This latter, in fact, is perfectly diamagnetic, as expected for Nb(V) (d^0). Its EPR spectrum is silent, against the presence of either Nb(IV) or a ligand-centered π-radical as well. Noticeably, the color of **I** is practically unchanged (light brown) and so is, accordingly, the UV−visible spectrum in solution of CH_2Cl_2, due to the quite peculiar persisting absence of the Q-band and to absorptions in the Soret region with position and intensity of the peaks present close to those of $(Pc)_2Nb$ (Table 1). The IR spectrum of **I** essentially resembles that of $(Pc)_2Nb$, with the most relevant difference consisting of the absence for the former of the central peak (ca. 1050 cm^{-1}) of the quintuplet present for $(Pc)_2Nb$ in the range 1100−1000 cm^{-1}.[6]

It should be also noted that the redox process $(Pc)_2Nb \rightarrow$ **I** is chemically reversible, since, by reduction with $NaBH_4$, **I** is readily reconverted into $(Pc)_2Nb$.

Structure of I. Crystal data and details associated with data collection and structure refinement for **I** are given in Table 2 and in Table S1 in the Supporting Information. Selected bond distances and angles are quoted in Table 3. Fractional atomic coordinates are listed in Table S2 for non-H atoms and in Table S3 for hydrogens. Thermal parameters are given in Table S4, and bond distances and angles are given in Table S5.[19]

Table 2. Experimental Data for the X-ray Diffraction Studies on Crystalline Complex **I**

compound	**I**
empirical formula	$C_{64}H_{32}N_{16}Nb{\cdot}I_3{\cdot}0.5I_2{\cdot}3.5C_{10}H_7Cl$
a	17.702(3) Å
b	18.708(3) Å
c	13.504(2) Å
α	106.00(2)°
β	93.39(2)°
γ	83.26(1)°
V	4267.5(13) $Å^3$
Z	2
fw	2194.8
space group	$P\bar{1}$ (No. 2)
t	22 °C
λ	0.710 69 Å
ρ_{calc}	1.708 g cm^{-3}
μ	17.35 cm^{-1}
R^a	0.079
$wR2^b$	0.207

[a] $R = \sum|\Delta F|/\sum|F_o|$, calculated on the unique observed data [$I > 2\sigma(I)$]. [b] $wR2 = \sum w|\Delta F^2|^2/\sum w|F_o{}^2|^{1/2}$, calculated on the unique total data with $I > 0$.

The main information from X-ray data on **I** can be summarized as follows:

(i) The structure consists of $[(Pc)_2Nb]^+$ cations (Figure 2), $(I_3)^-$ ions, I_2 molecules, and 1-chloronaphthalene molecules of crystallization in the stoichiometric molar ratio of 1/1/0.5/3.5.

(ii) The metal atom is in the center of the $[(Pc)_2Nb]^+$ cation and is surrounded by eight N atoms from the inner cores of the two phthalocyanine units (hereafter labeled A and B) arranged in the form of a square antiprism.

(iii) Two inter-ligand C−C σ bonds “staple” together the two phthalocyanine units (C11A−C11B, 1.574(15) Å; C31A−C31B, 1.574(15) Å).

(iv) The Pc ligands are in a staggered orientation (relative rotation about 45°, Figure 3).

(v) Each N_4 core shows remarkable tetrahedral distortion from the planarity ranging from −0.147(8) to 0.147(8) Å in A and from −0.137(8) to 0.098(7) Å in B, the metal being displaced by 1.164(1) and 1.154(1) Å, respectively, from the mean plane through the N1, N3, N5, and N7 nitrogen atoms.

(vi) The distance of the nearly parallel N_4 mean planes (dihedral angle 1.2(2)°) is 2.387(17) Å.

(vii) The Nb−N bond distances are different, those (Chart 1) involving the opposite N3 and N7 nitrogen atoms (average value 2.190(5) Å) being a little but significantly shorter than those involving the opposite N1 and N5 atoms (average value 2.249(11) Å). These values are a little longer than those observed in other mono(phthalocyanine) six- and seven-coordinate niobium complexes,[20,21] very likely as a consequence of the octacoordination of the metal. To our knowledge, there are no data reported in the literature for the comparison of these distances with those observed for other similar Nb sandwiched molecules.

It is noteworthy that the above features i−vii are practically coincident or very closely recall those observed for the “stapled” structure of Pc_2Ti.[2] It can be seen from Table 4 that both the

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Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex **I**

	molecule			molecule	
	A	B		A	B
Nb1−N1A	2.232(7)	2.237(8)	N4−C18	1.333(13)	1.321(13)
Nb1−N3A	2.190(7)	2.202(7)	N4−C21	1.309(14)	1.328(12)
Nb1−N5A	2.280(7)	2.243(7)	N5−C21	1.361(11)	1.367(11)
Nb1−N7A	2.186(8)	2.181(7)	N5−C28	1.428(12)	1.463(13)
N1−C1	1.365(13)	1.387(11)	N6−C28	1.269(12)	1.243(12)
N1−C8	1.450(11)	1.415(13)	N6−C31	1.429(10)	1.436(11)
N2−C8	1.254(14)	1.295(12)	N7−C31	1.531(11)	1.496(13)
N2−C11	1.428(13)	1.429(12)	N7−C38	1.311(13)	1.334(12)
N3−C11	1.482(11)	1.475(12)	N8−C1	1.295(12)	1.307(12)
N3−C18	1.345(12)	1.333(11)	N8−C38	1.357(11)	1.325(13)
C11A− C11B	1.574(15)				
C31A− C31B	1.574(15)				

	molecule A	molecule B		molecule A	molecule B
N1−Nb1−N3	74.7(3)	74.4(3)	N2−C11−N3	116.2(8)	118.2(8)
N1−Nb1−N7	74.2(3)	74.4(3)	N2−C11−C12	111.0(8)	110.3(8)
N3−Nb1−N5	74.3(3)	73.7(3)	N3−C11−C12	105.4(8)	104.0(7)
N5−Nb1−N7	73.9(3)	75.1(3)	N6−C31−N7	114.5(7)	117.7(8)
N1−Nb1−N5	110.2(3)	110.8(3)	N6−C31−C32	110.8(8)	109.8(8)
N3−Nb1−N7	123.4(3)	123.5(3)	N7−C31−C32	103.9(7)	104.0(7)

N2A−C11A− C11B	108.8(8)	N2B−C11B− C11A	107.9(8)
N3A−C11A− C11B	100.8(7)	N3B−C11B− C11A	101.9(8)
C12A− C11A− C11B	114.5(8)	C12B− C11B− C11A	114.6(8)
N6A−C31A− C31B	111.8(8)	N6B−C31B− C31A	108.6(8)
N7A−C31A−C31B	99.7(7)	N7B−C31B− C31A	101.0(8)
C32A−C31A−C31B	115.5(8)	C32B− C31B− C31A	115.8(8)

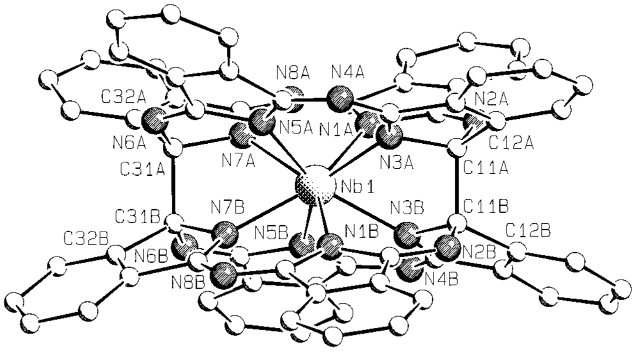

Figure 2. SCHAKAL side view of the $[(Pc)_2Nb]^+$ cation in complex **I**.

average M−N bond distances and the distance between the N_4 planes of $[Pc_2Nb]^+$ are comparable to those of Pc_2Ti; interestingly, however, the distance between the N_4 planes of $[Pc_2Nb]^{+1}$ more closely approaches that of the "unstapled", though still highly distorted, $[Pc_2Ti]^{+0.66}$ and Pc_2Zr, whereas the difference is much more consistent with those of the other "normal" sandwiched species.

As shown below in paragraphs viii−xi, a more detailed examination of the X-ray data indicates that the structural similarity of $[Pc_2Nb]^+$ and Pc_2Ti moves even further (for a better comparison, the labeling scheme adopted in Chart 1 for the two crystallographically independent Pc moieties in $[Pc_2Nb]^+$ is consistent with that used for $(Pc)_2Ti$[2]).

(viii) As already observed for $(Pc)_2Ti$, the inter-ligand C−C bond distances are just a little longer than expected for normal $C(sp^3)−C(sp^3)$ σ bonds.

(ix) Due to the sp^3 character of the C11 and C31 carbon atoms, the planarity of the Pc ligands is completely removed, as indicated by the bending of the isoindole units with respect to the N_4 core and by the "twisting" of the external phenyl rings (see data reported in Table S6a,b). These two aspects were already considered in detail for $(Pc)_2Ti$ (see pertinent data reported in Table 2 of ref 18) and are not discussed further here.

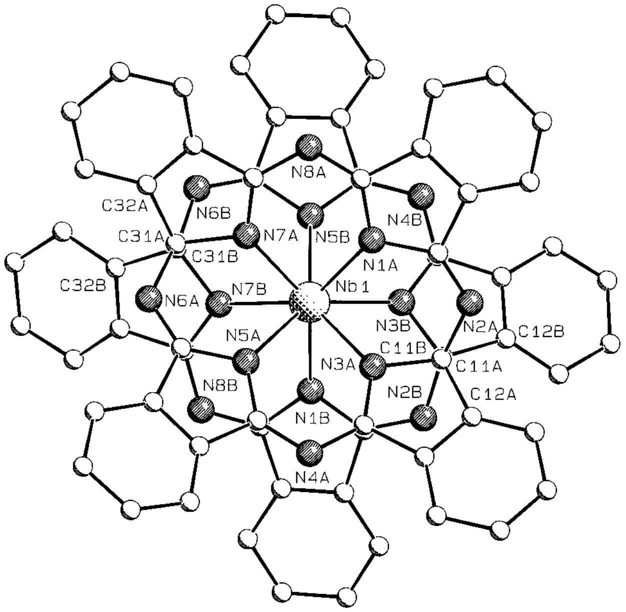

Figure 3. SCHAKAL top view of the $[(Pc)_2Nb]^+$ cation in complex **I**.

(x) The formation of the two inter-ligand C−C σ bonds corresponds to the breaking of one out of the nineteen π bonds in each "normal" phthalocyaninato unit and should be seen as an isomerization process and not as a redox one, as discussed in detail in the parallel case of $(Pc)_2Ti$ (see Figure 3 in ref 2).

(xi) The values of bond distances within the N1,C8,N2,C11,N3 and N5,C28,N6,C31,N7 chelation rings are consistent with a double bond character of the N2−C8 and N6−C28 bonds, while those within the N1,C1,N8,C38,N7 and N3,C18,N4,C21,N5 chelation rings are consistent with the delocalization of two double bonds (Table 3).

In conclusion, the above information on the cationic fragment $[(Pc)_2Nb]^+$ and that known for the parallel species $(Pc)_2Ti$ unequivocally indicate that (1) the unoxidized species $(Pc)_2Nb$

Chart 1. Labeling Scheme Adopted for the Pc Ligand in **I**

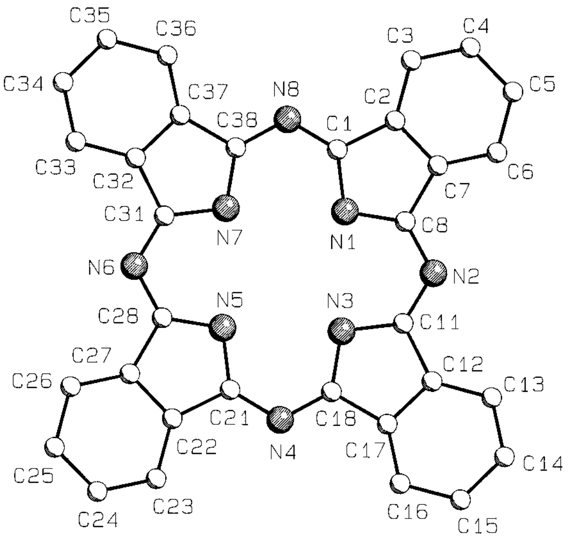

Table 4. Crystal Data on Bis(phthalocyanine) Metal Complexes

complex	average M−N (Å)	distance between N_4 planes (Å)	relative rotation (deg)	ref
$[Pc_2Ti]$	2.22	2.32	45	2
$[Pc_2Nb]^+$	2.22	2.387	45	this work
$[Pc_2Ti]^{+0.66}$	2.246	2.42	41.1	18
$[Pc_2Zr]$	2.30	2.52	42	18, 4
$[Pc_2Sn]$	2.35	2.70	42	5b
$[Pc_2U]$	2.43	2.81	37	22
$[Pc_2Nd]$	2.44	2.96	45	23
$[Pc_2Lu]$	2.40	2.69	49	24

is also a "stapled" sandwiched form, the molecular shape being very close to that of its corresponding monoelectronically oxidized analogue; (2) the process leading from $(Pc)_2Nb$ to $[(Pc)_2Nb]^+$ implies a metal centered Nb(IV) → Nb(V) monoelectronic oxidation; and (3) this work represents one step forward toward the synthesis and characterization of metal bis(phthalocyanine) complexes showing two inter-ligand C−C σ bonds, an extreme distortion of the Pc units, with associated considerable loss of π electron delocalization and exclusive UV−visible spectral features.

The structural analysis revealed the presence in the unit cell of four crystallographically independent iodine atoms (Figure 4), doubled through a center of symmetry lying just between I4 and I4′ atoms. Such an arrangement suggests an I_8^{2-} fragment, composed of two peripheral unsymmetrical I_3^- ions (average bond distance for the couples I1−I2 and I2−I3, 2.905 Å, which is close to 2.920 Å, the value for symmetrical I_3^- ; see ref 25) and one central I_2 molecule (I4−I4′, 2.752(2) Å; 2.712 Å in crystalline I_2; see ref 26). If the internal bond distances are accurately considered, the most appropriate description of the bridged system can be of the type $(I_2{\cdots}I^-){\cdots}I_2{\cdots}(I^-{\cdots}I_2)$. The Raman spectrum of the species is considerably disturbed by fluorescence effects due to the presence of the ClNP molecules in the crystals of **I**. As a consequence, the spectrum, although not in contrast with the structural findings, is not particularly informative, as it shows in the region 200−100 cm^{-1} only one neat peak located at 167 cm^{-1}, possibly due to ν(I−I) of the external I_2 molecules elongated by the interaction with I^- ions.

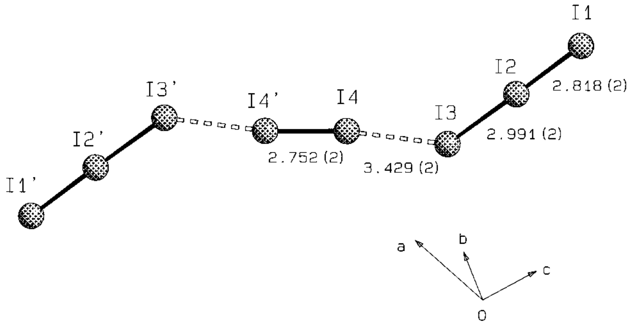

Figure 4. SCHAKAL projection showing the chaining among (I_3^-) anions and the centrosymmetric I_2 molecule. Prime denotes a transformation of $1 - x$, $1 - y$, $-z$.

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Supporting Information Available: Six tables giving crystal details of the structure determination, fractional atomic coordinates, anisotropic and isotropic thermal parameters, bond lengths and bond angles, and ORTEP and SCHAKAL drawings (Figures S1 and S2) showing the $[(Pc)_2Nb]^+$ cation in complex **I**; also included in Table S6 are details about the bending of the isoindole groups with respect to the N_4 chromophore and twisting of the peripheral phenyl rings (17 pages). Ordering information is given on any current masthead page.

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