Notes

Electron Energy Level Transitions in Bis(phthalocyaninato)titanium(IV) Examined by UV−Visible, Near-IR, EELS, and XPS Spectra

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The recently reported titanium(IV) diphthalocyanine complex $Pc_2Ti\cdot ClNP$ (Pc = phthalocyaninato dianion, $C_{32}H_{16}N_8^{2-}$; ClNP = α-chloronaphthalene) shows Ti(IV) in the center of the sandwich molecule, surrounded by the eight inner N atoms of the two Pc units arranged in a square antiprismatic fashion (Figure 1).[1] The complex represents a unique example of a diphthalocyanine metal complex in which the two macrocyclic rings are "stapled" together by two interligand C−C σ bonds. This structural feature highly affects the extended π-electron delocalization normally present in the phthalocyanine macrocycle. As a consequence, no absorptions are shown in the Q visible region by the solution spectra of this Ti complex in ClNP,[1] in striking contrast with the observed visible spectral behavior of "normal" phthalocyanine systems.[2]

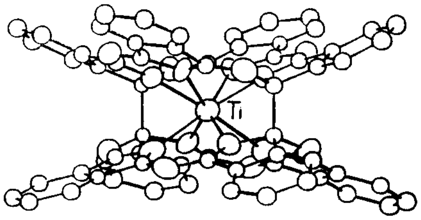

Figure 1. Side view of Pc_2Ti. Reprinted with permission from ref 1. Copyright 1990 Royal Society of Chemistry.

The sandwich molecules in the crystal lattice of $Pc_2Ti\cdot ClNP$ are far apart from one another, which is different from the linearly elongated cofacial arrangement found for the β and α forms of simple metal phthaloycanines, PcM (M = bivalent first transition series metal ion), which is a prerequisite for good electrical conduction properties, as is indeed observed, for instance, for several PcM α-forms.[3] Thus, $Pc_2Ti\cdot ClNP$ is a nonconducting material, as is also the structurally analogous, though "unstapled", $Pc_2Sn\cdot ClNP$.[4] Upon iodine doping, both these Ti and Sn complexes form columnarly stacked isomorphous materials having the formula Pc_2MI_2 (M = Ti(IV), Sn(IV)), more correctly formulated as $[Pc_2M](I_3)_{0.66}$.[5] These materials show highly enhanced electrical conductivity, with σ_{RT} values in the range 10^{-4}−10^{-2} Ω^{-1} cm^{-1}, typical of semiconducting systems. Noticeably, the iodine doping of the Ti complex implies the breaking of the interligand C−C σ bonds, and the phthalocyanine chromophore is, at least partially, recovered.[5]

In the present contribution, UV−visible and near-IR, EELS, and XPS spectra of Pc_2Ti are presented, and the description of the Ti(IV) 3d level distribution is attempted. Some pertinent information is also achieved on the Sn analog. Further work is in progress in an attempt to achieve a deeper understanding of the spectroscopic and electrical conductivity properties of the corresponding partially oxidized Pc_2MI_2 species (M = Ti, Sn).

Experimental Section

All samples of $Pc_2Ti\cdot ClNP$ and its Sn analogue were preliminarly sublimed under vacuum, with an implied elimination of ClNP.

UV−visible and near-IR spectra were recorded on a Cary 5 spectrometer. XPS and EELS measurements were performed in a high vacuum (HV) apparatus (VG ESCA MK2) with a chamber equipped with an electron gun for Auger and energy-loss experiments. For the XPS spectra use of made of a Al $K\alpha_{1,2}$ source. For the EELS measurements, which were obtained at liquid nitrogen temperatures to improve resolution, the adopted incident energy was $E_p = 200$ eV, with a peak-to-peak modulation of 1.0 eV. Thin films of Pc_2Ti, obtained by evaporation on quartz windows, were used for the absorption spectra in the region 200−1500 nm, due to the high intensity of the observed peaks. Pressed pellets of pure samples of Pc_2Ti and Pc_2Sn were instead used for the electron-energy-loss (EELS) experiments and also for the reflectance spectra in the region 800−2000 nm, since in this latter region the intensity of the observed absorptions is low.

Results and Discussion

In simple metal phthalocyanines of formula PcM (M = bivalent metal ion) as well as in the free macrocycle, PcH_2, the presence of the extended π-electron delocalization flowing along the ligand gives rise to two main UV−visible absorptions in the regions 600−700 and 300−400 nm. They are the electronic origin of the first (Q band) and the second (Soret band) excited singlet states, respectively, and are assigned as π−π^* transitions. In light of this, two aspects need to be claimed in the case of the sandwiched Pc_2Ti: (a) The bonding orbitals of the octacoordinated Ti(IV) involved in this system are the 3d, 4s, and 4p orbitals, which, undergoing hybridization, form the eight orbitals bound to the N 2p orbitals of the ligand; (b) the interligand C−C σ-bonds strongly bend the two macrocycles, significantly affecting the electron delocalization in both macrocycles. The remarkable effect is the disappearance in the visible solution spectrum in ClNP of the characteristic Q-band.[1]

In terms of a band structure model, particular attention is paid to the energetic position of the unoccupied Ti 3d-like levels lying near the Fermi level (E_F). In connection with this, we find useful here to refer to the meaningful analysis developed by different authors,[6−8] both theoretically and experimentally, on a series of Ti(IV) dichalcogenides. In these layered solid

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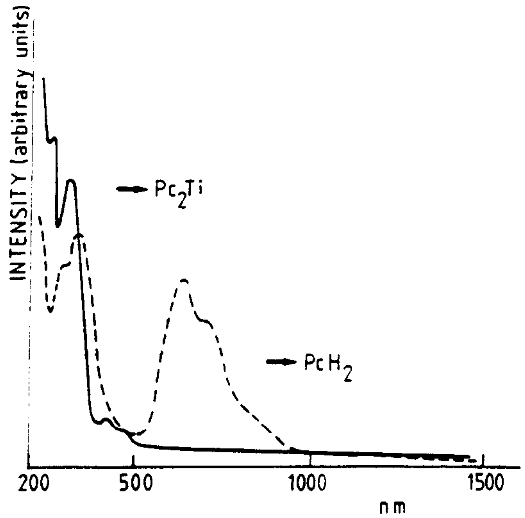

Figure 2. Absorption spectra of evaporated films of Pc_2Ti and PcH_2 in the region 200−1500 nm.

materials, the metal centers are octahedrally surrounded by six chalcogen atoms arranged in a more or less distorted trigonal prismatic symmetry. In this series of complexes the electronic distribution around the Fermi level has been proposed by Drube *et al.*[7] as follows: "the valence band is based primarily on a bonding combination of chalcogen-p and Ti-s states. This band is separated by its antibonding counterpart by a gap of several electron volts. 'Within' this gap lie the rather localized Ti-3d bands." In spite of the structural difference occurring between this class of chalcogenides and the species dealt with here, a similar energy level distribution may be supposed. If this is accepted, then the energetic position of the Ti 3d-like levels in Pc_2Ti should be found in the red edge of the missing Q band, i.e. between 700 and 1500 nm.

Figure 2 shows the absorption visible spectrum of an evaporated film of Pc_2Ti in the specific region where the Q and Soret (B) bands are normally observed (200−1000 nm), and the spectrum of PcH_2 for comparison. In keeping with previous findings in ClNP solution,[1] the absence, in the expected region (600−700 nm), of the Q band, associated with the $\pi-\pi^*$ transition concerning the "inner" ring π system, is confirmed here also for solid Pc_2Ti. Noticeably, in the case of Pc_2Sn, since its structure is normal, i.e. "unstapled", it shows, coherently, both the Q and the Soret bands. Due to the lack of the Q band for Pc_2Ti, the assignment of the two strong absorptions located at 306 and 250 nm as being due to the Soret transition does not appear straightforward; a possible partial presence of such transition may be justified if it is considered that this transition ($\pi-\pi^*$ in the macrocycle) also involves the "outer" part of the ring system, because of the existence of some overlap[9] between the a_{2u} and e_g orbitals of the external essentially unperturbed phenyl rings. It should be claimed, however, that the Soret region is the site where the first ligand-to-metal transitions are also observed (see below, EELS and XPS spectra).

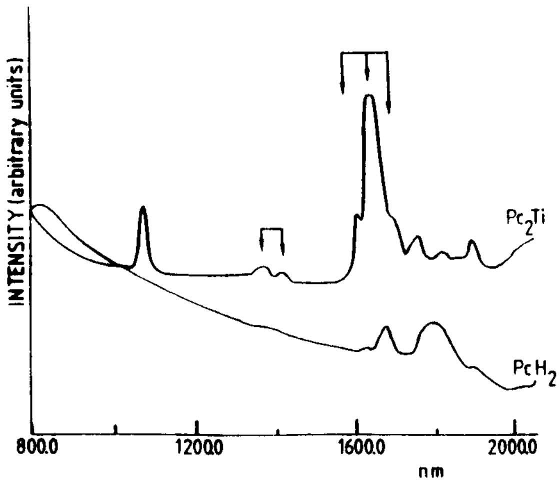

Figure 3. Reflectance spectra of pressed pellets of Pc_2Ti and PcH_2 in the region 800−2000 nm.

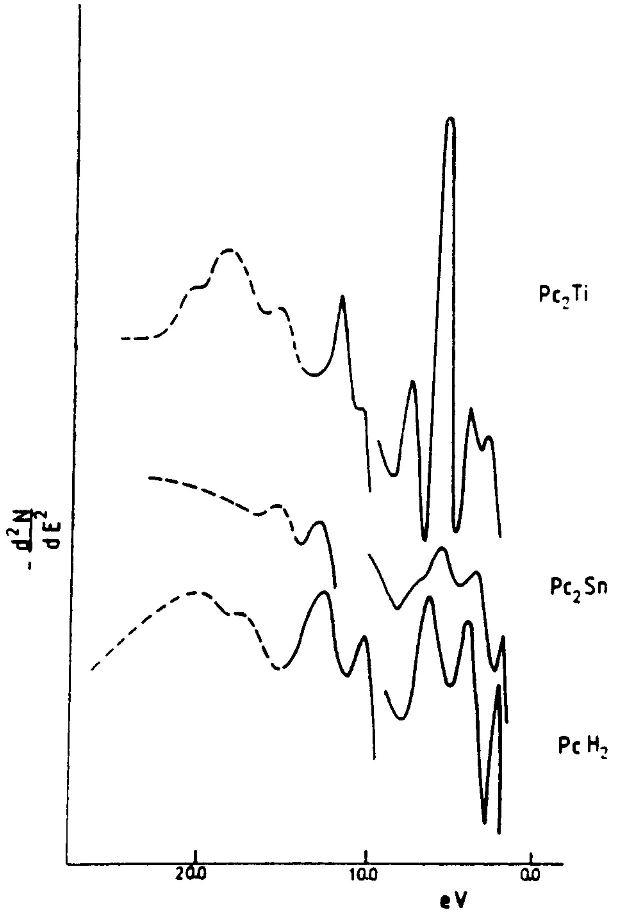

Figure 4. EELS spectra of Pc_2Ti, Pc_2Sn, and PcH_2 at −180 °C. E_p = 200 eV.

Figure 3 shows the reflectance spectra taken on pressed pellets of Pc_2Ti and PcH_2 in the region 800−2000 nm, where the absorptions associated with the Ti 3d orbitals are expected to be found. In the spectrum of Pc_2Ti a well-identified triplet is present with peaks at 1635, 1670, and 1720 nm. This triplet is not observed in PcH_2, although in this latter compound a weak absorption is found in that zone, very likely of a different nature. The triplet is reasonably attributed to transitions to the t_{2g} levels of Ti 3d. In this context, when the distortion around Ti is adequately considered, the two next very weak peaks observed at 1370 and 1410 nm may be assumed as being due to transitions to the Ti 3d e_g doublet. Finally, the isolated peak observed at 1140 nm may be assigned to the n → Ti e_g transition (n = nonbonding orbital of the coordinated nitrogen).

In Ti(IV) (d^0) compounds, the first interband transitions are ligand-to-metal in nature. These transitions can be evidenced

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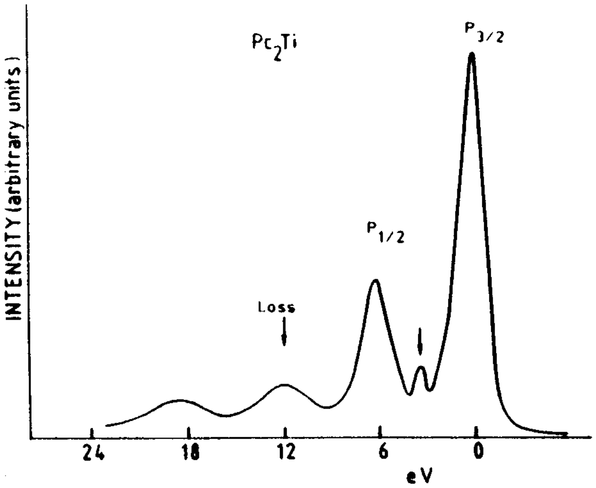

Figure 5. XPS spectrum of Pc$_2$Ti in the Ti 2p region.

by means of the electron-energy-loss spectroscopy (EELS) in the region near to the primary beam. For comparison, the low temperature (−180 °C) EELS spectra of Pc$_2$Ti together with those of PcH$_2$ and Pc$_2$Sn are shown in Figure 4. At about 2.0 eV a net exciton-like peak is observed for PcH$_2$ overlapping with the first interband transition at about the same energy.[3] The same exciton is present in Pc$_2$Sn, but not in Pc$_2$Ti.

The first interband transitions observed in EELS at 3.2, 4.2, and 5.8 eV for Pc$_2$Ti and at 3.5 and 5.7 eV for Pc$_2$Sn are assigned to the first ligand-to-metal transitions, differently from Tada *et al.*[10] (see for this our work in ref 3 and references therein). Remarkably, the absorption observed at 4.2 eV for Pc$_2$Ti lies in the same spectral region where the two UV−visible absorptions are observed at 4.05 and 4.9 eV (306 and 250 nm, respectively). The close positioning of these absorptions is the reason why the assignment of the latter bands as Soret transitions is made uncertain (see previous discussion). The fact that only one absorption is found at 4.2 eV, instead of two distinct peaks, does not eliminate the problem, since minor resolution is normally allowed by the EELS technique. Other higher interband transitions appear in the EELS spectrum at 7.7 and 10.7 eV, while the bands present in the region 12.0−21.0 eV should be plasma oscillations of the valence electrons (plasmons). The XPS spectrum of Pc$_2$Ti (Figure 5) offers some additional information about the first interband transitions, essentially confirming the EELS results. In particular, the Ti 2p zone of the spectrum shows, together with the main transitions (2p), one satellite located at ca. 3.4 eV from the main peak Ti 2p $^3/_2$, which confirms the presence of an interband transition at this energy, and one broad satellite (clearly a plasmon) at 12.0 eV from each of the two Ti 2p $^3/_2$ and Ti 2p $^1/_2$ main peaks, which corresponds to the same transition observed in EELS.

Conclusions

Examination of UV-visible and near-IR, EELS, and ESCA spectra of Pc$_2$Ti and Pc$_2$Sn allows the following conclusions to be drawn.

(a) The “stapled” Pc$_2$Ti shows two inter-ligand C-C σ bonds, with considerable distortion of the Pc units. The consequence is the disappearance of the Q bands in the 600−700 nm visible region. This spectral anomaly has required a reexamination of the assignments in both the Q and Soret regions.

(b) It is possible to observe, by UV−visible and near-IR spectroscopy, the energetic position of the empty Ti 3d levels of Pc$_2$Ti, in which Ti(IV) is in the centre of a distorted square antiprism.

(c) The EELS and XPS spectra allow one to observe the first ligand-to-metal transitions and some plasma oscillations of the valence electrons (plasmons).

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