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Synthesis and Solution Spectral Properties of Antimony(III) Phthalocyanine and Dihydroxoantimony(V) Phthalocyanine Complexes

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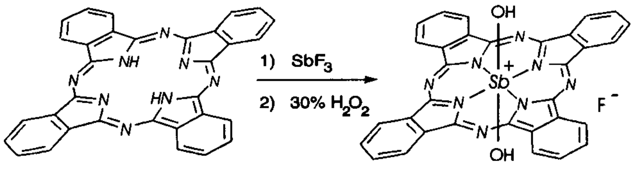
Introduction

Ever since their accidental discovery early this century, the phthalocyanine molecule $H_2(Pc)$ and its derivatives have been among the most intensely studied macrocyclic compounds in dyestuff and coordination chemistry.[1] More recent research developments include unique applications of phthalocyanines and metallophthalocyanine complexes in materials science,[2] medicine,[3] electrochemistry, and photocatalysis.[4] The electronic spectra of many metallophthalocyanines quite closely resemble the absorption properties of natural photosynthetic pigments like chlorophylls and bacteriochlorophylls, and their potential use as photosensitizers for the collection and storage of solar energy has been investigated.[5] While progress in this latter field remains in its infancy, it seems clear now that the creation of any practical "artificial photosynthetic" system will require a very efficient combination of both light harvesting and multielectron catalysis.[6] One of the promising new strategies to overcome the problems of accumulating multiple redox equivalents is the reversible photochemical interconversion of low- and high-valent main group metal catalysts.[7] In this context, our studies on antimony porphyrin complexes have been extended toward the phthalocyanine sensitizer family. Although antimony phthalocyanines had already been prepared in the pioneering works of Linstead et al.,[8] almost nothing is known about the chemical and physical properties of these compounds so far.[9−11] Phthalocyanine complexes containing the group 15 central atoms bismuth and phosphorus have previously been investigated in some detail.[12,13] The present study was undertaken to characterize the catalytically more relevant antimony derivatives in solution.

Scheme 1. Formation of $[(Pc)Sb^V(OH)_2]F$ Starting from Free Base Phthalocyanine



Experimental Section

Phthalocyanine (Strem Chemicals), antimony(III) fluoride (Merck), and aqueous hydrogen peroxide solution (Merck) were applied as purchased without further purification. Acetone was freshly distilled prior to use. All photophysical experiments were carried out in spectrograde solvents. Absorption spectra were recorded with a Uvikon 860 double-beam spectrophotometer using 1-cm quartz cells. A Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier was used to obtain luminescence spectra, which were corrected for monochromator and photomultiplier efficiency.

Synthesis of the desired low- and high-valent metallophthalocyanines was achieved in a straightforward reaction sequence (Scheme 1) according to established routes.[14] When free base phthalocyanine was cautiously heated with an excess of SbF_3 (10 equiv), the solids rapidly fused to a dark green mixture. Methanol extraction of this crude material yielded the green antimony(III) phthalocyanine complex [(Pc)Sb]F, while the bluish-green dihydroxoantimony(V) derivative $[(Pc)Sb(OH)_2]F$ was obtained after treatment of the reaction mixture with stoichiometric amounts of 30% hydrogen peroxide, subsequent acetone extraction, and filtration over dry silica gel.[15] The antimony(V) derivative shows a gradual aging process, which is connected with a strong decrease in solubility. Most probably, as reported for other main group (phthalocyaninato)metal complexes,[2] this compound undergoes an axial polycondensation reaction that leads to oxo-bridged oligomers.

Results and Discussion

Both reduced and oxidized forms of the antimony phthalocyanine complexes investigated in this study are readily soluble in polar media like alcohols, acetone, or acetonitrile. Although ion migration tests have not been carried out, this behavior, together with mass spectral data,[15] strongly suggests a formulation as cations $[(Pc)Sb^{III}]^+$ and $[(Pc)Sb^V(OH)_2]^+$ in analogy to the related group 15 metalloid porphyrins.[9] The redox conversion between the low- and high-valent complexes can be followed spectrophotometrically, as shown in Figure 1. Several isosbestic points indicate that this net two-electron transformation proceeds in a clean and quantitative reaction.

The absorption spectral properties of monomeric antimony(III) phthalocyanine and dihydroxoantimony(V) phthalocyanine in ethanol solution are displayed in Figure 2 and summarized in Table 1. Tetrapyrrole-type macrocycles with main group central atoms in lower oxidation states frequently show pronounced metal-to-ligand charge transfer (MLCT) transitions in the visible region of their spectra.[9] This is also the case with antimony(III) phthalocyanine, whose absorption features are best

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(15) $[(Pc)Sb^{III}]F$: FD-MS *m/z* 633.0 ($C_{32}H_{16}N_8{}^{121}Sb^+$); $[(Pc)Sb^V(OH)_2]F$: FD-MS *m/z* 667.0 ($C_{32}H_{18}N_8O_2{}^{121}Sb^+$).

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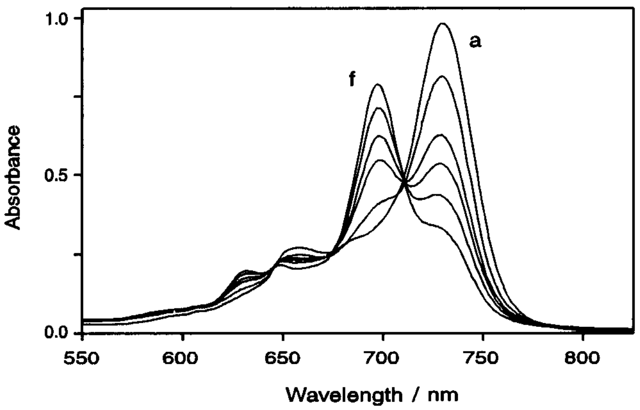

Figure 1. Spectral changes during the oxidation of 5.7×10^{-6} M [(Pc)-Sb^{III}]F in the presence of 10^{-2} M H_2O_2 at (a) 0, (b) 1, (c) 2, (d) 3, (e) 5, and (f) 15 min reaction times (acetone, 298 K).

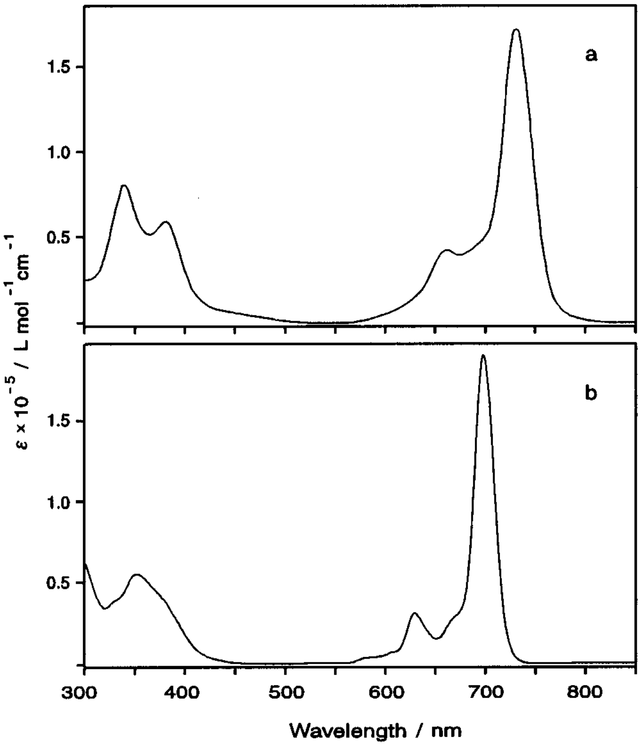

Figure 2. Electronic absorption spectra of (a) [(Pc)Sb^{III}]F and (b) [(Pc)-Sb^{V}(OH)$_2$]F in ethanol.

Table 1. Absorption Data for (a) [(Pc)Sb^{III}]F and (b) [(Pc)Sb^{V}(OH)$_2$]F in Ethanol

compd	λ_{max}/nm (10^{-3} ϵ/L mol^{-1} cm^{-1})
a	257 (66.1), 338 (81.4), 381 (59.8), 660 (42.6), 729 (171.7)
b	298 (64.0), 350 (56.5), 385 (37.7), sh 628 (32.6), 699 (190.8)

described as an irregular "hyper" spectrum[16] with both B (Soret) and MLCT bands in the 300−500-nm region, together with a red-shifted Q band maximum at 729 nm (Figure 2a). In contrast, the dihydroxoantimony(V) complex (Figure 2b) shows a regular $\pi-\pi^*$-dominated absorption spectrum, which is characteristic of a nonaggregated, diamagnetic metallophthalocyanine.[1]

To examine the luminescence properties of the antimony phthalocyanines, dilute spectrograde ethanol solutions were thoroughly purged with argon and measured at room temperature. No authentic emission could be observed for the low-valent [(Pc)Sb]F complex. In some samples, however, traces of free base phthalocyanine were identified by its strong red fluorescence at 696 nm and by its characteristic Q band excitation spectrum. The room temperature emission and excitation spectra of the antimony(V) derivative [(Pc)Sb(OH)$_2$]F in deaerated ethanol are shown in Figure 3. Corresponding energies, quantum yields (ϕ), and calculated lifetimes (τ) are listed in Table 2. Dihydroxoantimony(V) phthalocyanine exhibits a moderately strong red fluorescence from the lowest excited singlet state. The $S_1 \rightarrow S_0$ emission spectrum is an approximate mirror image of the Q absorption band pattern (Figure 2b), and the Stokes shift of the emission maximum is rather small. As shown in Figure 3, the fluorescence excitation spectrum agrees very well with the absorption spectrum of the compound. Even though the $T_1 \rightarrow S_0$ phosphorescence of the [(Pc)Sb(OH)$_2$]F complex cannot be detected at 298 K, an estimated triplet energy of 104 kJ mol^{-1} (1150 nm) is obtained from the electronic origin of the S_1 fluorescence and the S_1−T_1 energy gap usually observed[20] for regular metallophthalocyanines. This triplet energy value is higher than the energetic limit[3] of about 94 kJ mol^{-1} (1270 nm) necessary for a photosensitized generation of singlet ($^1\Delta$) molecular oxygen.

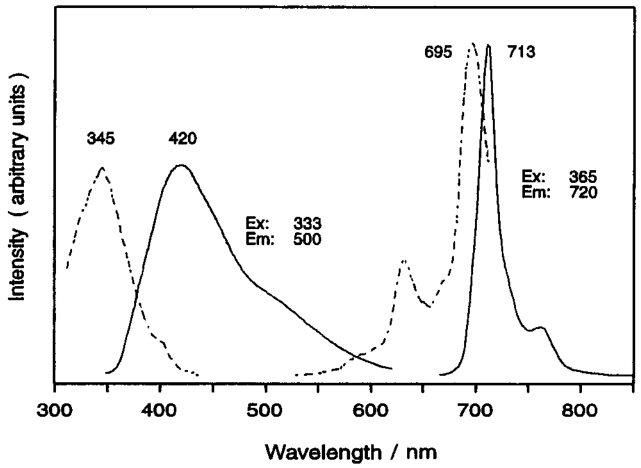

Figure 3. Fluorescence emission (solid lines) and excitation spectra (broken lines) of [(Pc)Sb^{V}(OH)$_2$]F in argon saturated ethanol at 298 K. Excitation and emission wavelengths used to record the spectra are shown.

Table 2. Photophysical Properties of [(Pc)Sb^{V}(OH)$_2$]F in Ethanol at 298 K

parameter[a]	S_1 emission	S_2 (Soret) emission
E_{0-0}/cm^{-1}	14 200	26 400
Stokes shift/cm^{-1}	300	4800
τ°_{rad}/ns	6.9	1.5
τ_F/ns	0.5	0.1
ϕ_F	0.076[b]	0.071[c]

[a] Lifetime values were estimated according to the method of Strickler and Berg.[17] [b] Fluorescence quantum yield relative to EuTTA standard.[18] [c] Quinine sulfate standard.[19]

Besides this quite "normal" behavior, the photophysical properties of the antimony(V) derivative are remarkable in that a conspicuous blue luminescence with a maximum at 420 nm is observed upon ultraviolet excitation of [(Pc)Sb(OH)$_2$]F in ethanol solution (Figure 3). Well-documented examples of

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anomalous upper excited state emission in condensed phases are extremely rare,[21] and knowledge on the so-called S_2 fluorescence of phthalocyanines[22] is still very limited. The occurrence of $S_2 \rightarrow S_0$ emission is presumed to be possible due to the relatively large S_2-S_1 energy gap of 12 200 cm^{-1} (Table 2), which should considerably slow down the radiationless decay process of the upper excited singlet state.[21] Apart from its much higher quantum yield, the characteristics of the observed blue $[(Pc)Sb(OH)_2]F$ luminescence resemble closely those reported recently for a series of zinc phthalocyanine analogues.[22] The S_2 emission band is broad and rather structureless and exhibits a large Stokes shift. As shown in Figure 3, the corresponding fluorescence excitation spectrum closely matches the $S_0 \rightarrow S_2$ (Soret) absorption band of the compound in both shape and energy.

In summary, the present study for the first time gained some information on the redox chemistry and electronic spectroscopy of low- and high-valent antimony phthalocyanines. Future investigations will focus on potential applications of these compounds in the fields of photosensitization and photoredox catalysis.

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