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Synthesis and Characterization of a Phthalocyanine-Porphyrazine Hybrid and its Palladium(II) Complex

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Summary. A phthalocyanine-porphyrazine hybrid molecule composed of three phthalonitrile units and one maleonitrile moiety was prepared by cyclomerization of the reactants in the presence of magnesium butoxide. Two thioether groups fused to β-pyrrol positions were complexed with $PdCl_2$. The compounds were characterized by ^1H NMR, IR, and UV/Vis spectroscopy as well as elemental analysis.

Keywords. Macrocycles; Complexes; Palladium; Phthalocyanine; Porphyrazine.

Introduction

As in the case of phthalocyanines, functionalization of the porphyrazine core at the periphery has attracted increasing attention during the last decade [1, 2]. Whereas early efforts were mainly directed towards symmetrically substituted derivatives, the construction of unsymmetrical structures made up of unsaturated 1,2-dinitriles and phthalonitriles has been developed later [3]. In this context, *Hoffmann* and *Barrett* have provided examples of heteroatom donors directly bound to the macrocyclic core of the porphyrazine side of the hybrid structure [3–6].

In addition to the peripherally functionalized phthalocyanine derivatives, we have recently focused on the preparation of novel porphyrazines, making use of the liability of substituted dithiomaleonitriles to cyclotetramerize in the presence of magnesium alkoxide [7–11]. We have accomplished to prepare symmetrically *octakis*-substituted derivatives with active peripheral substituents, among them crown ethers [12], ferrocenes [13], dimethylamine, and trimethylammonium groups [14].

Despite the growth of research currently being carried out world-wide on the synthesis of phthalocyanines and porphyrazines with thioether substituents, to our knowledge complexation of these donors with palladium(II) has been investigated only in the solution state, and no product has been isolated [15, 16]. Complexes of thioethers with Pd(II) have been investigated in detail in the case of thiacyclophanes [17]. In the present article we report on the synthesis of a new metal-free phthalocyanine-porphyrazine hybrid structure and its palladium(II) complex on the peripheral thioether donors directly bound to the 18-Π electron containing inner core.

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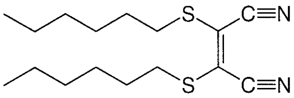
Results and Discussion

The synthesis of phthalocyanine-porphyrazine hybrid structures started with the cocyclization of *bis*-hexylthio-maleonitrile (**1**) with phthalonitrile (**2**) [18–19]. Generally, six reaction products would be expected involving six possible structures with the ratio of **1**:**2** ranging from 0:4 to 4:0 [20]. In order to make use of both the insolubility of all phthalonitrile products (*i.e.* the phthalocyanines) and the solubility of hexylthio substituted products, the ratio of **1**:**2** was kept sufficiently small to direct the reaction to form derivatives containing mainly phthalocyanine systems and only a single maleonitrile unit. Demetalization of these products with a strong acid (*e.g.* trifluoroacetic acid) yielded the insoluble metal-free phthalocyanine (H_2Pc) together with a sufficiently high amount of the soluble phthalocyanine-porphyrazine hybrid (**3**).

The four-coordinate palladium complex **4** was prepared by substitution of the benzonitrile moieties of *bis*-benzonitrile-palladium dichloride with **3** to form a five membered chelate ring. The square planar complexation of the type $PdCl_2S_2$ did not cause apprecible change in the colour of the macrocycle due to the intense absorption of the 18-Π electron system.



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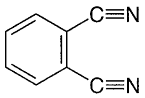

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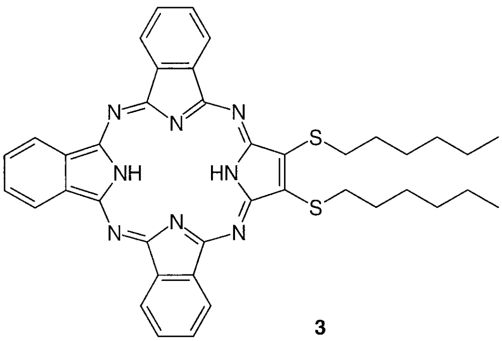

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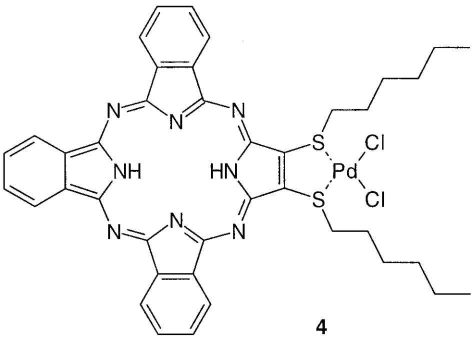

4

The IR spectrum of **3** showed NH streching vibrations of the inner core at 3270 cm^{-1} and CH vibrations of the hexyl groups around 2840–2900 cm^{-1}. After complexation with palladium(II), the presence of the inner core NH groups was verified by the NH streching absorptions around 3260 cm^{-1}. The ^{1}H NMR spectra of **3** and **4** also confirm the metal-free state for both structures. The chemical shift for the NH group in **3** appeared at −4.0 ppm as a broad peak which is a typical value for porphyrinoid structures [1–5]. In **4**, these protons are shifted to −1.3 ppm. The aromatic protons of **3** were observed between 8.13 and 7.39 ppm as a singlet, a doublet, and a triplet. These peaks also shifted to 8.87-7.97 ppm after complexation. For the S-CH_2 protons of **3** and **4**, a highfield shift of 0.14 ppm was observed upon complexation.

The electronic spectra of phthalocyanines and porphyrazines do not extensively change in their general appearance upon peripheral subtitution, but removal of one benzo group causes noticeable differences. A single Q band in metallo derivatives and its splitted form in their metal-free counterparts are characteristic [2]. A comparison of metal-free phthalocyanine with the metal-free porphyrazine indicates that the splitted Q bands are extremely broad and of low intensity in the latter. In this sense, the UV/Vis spectrum of the metal-free phthalocyanine-porphyrazine hybrid **3** resembles that of metal-free phthalocyanine. However, the position of the absorption maxima indicates a structure of lower symmetry than D_{2h}. As shown in Fig. 1, the splitted intense peaks appear at 616 and 708 nm, clearly separated in contrast to metal-free phthalocyanine, and there are two less intense peaks at 654 and 676 nm in between. The result of complexation with etheral S-donors was expected to cause apparent changes in the UV/Vis spectrum, since these heteroatoms are in direct contact with the aromatic Π-electron system. This should lead to a clear difference with respect to complexation of donor groups on the periphery of phthalocyanine, where complexation affects the electronic spectra only indirectly by enhancing or diminishing the aggregation of planar molecules. From Fig. 1, only slight broadening of the B band can be observed, but the Q band region

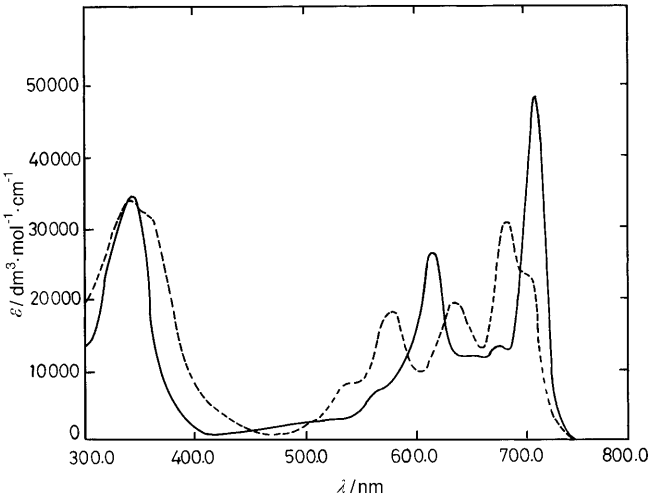

Fig. 1. UV/Vis of phthalocyanine-porphyrazine hybrid **3** (—) and its $PdCl_2$ complex **4** (- - - - -)

is completely different for **4**. Three peaks at 579, 637, and 684 nm together with a shoulder at 703 nm indicate that the symmetry of the molecule has changed and that the planar coordination sites around palladium(II) are no longer located in the plane of the macrocycle.

Experimental

IR spectra were recorded on a Mattson 1000 FTIR spectrometer using KBr pellets. UV/Vis spectra were measured on a UNICAM UV/Vis spectrophotometer. ^{1}H NMR spectra were acquired on a Bruker 250 MHz spectrometer. Elemental analyses were carried out by the analysis laboratory of the Tübitak Marmara Research Center; the results were in good agreement with the calculated values. 1,2-*Bis*-hexylthio-maleonitrile [18, 19] and *bis*-benzonitrile-palladium dichloride [21] were prepared according to literature procedures.

22,23-Di(hexylthio)-μ-27H,29H-tribenzo[b,g,l]porphyrazine (**3**; $C_{40}H_{40}N_8S_2$)

Mg powder (312 mg, 13 mmol) was refluxed overnight in 50 cm^3 of butanol with the addition of a few crystals of I_2. To this mixture, 310 mg *bis*-hexylthio-maleonitrile (1 mmol) and 3.2 g phthalonitrile (25 mmol) were added, and the mixture was refluxed for 12 h under N_2. A dark-blue suspension was obtained. After filtration, the filtrate was evaporated to dryness. The crude product was demetallized with 5 cm^3 of CF_3COOH and treated with 10 cm^3 methanol to precipitate the product. After filtering, washing with methanol, and drying, the solid product mixture was treated with 15 cm^3 $CHCl_3$, stirred for 1 h, and then filtered in order to separate the desired product from the insoluble metal-free phthalocyanine. Evaporation of the solvent to dryness and addition of 10 cm^3 methanol resulted in a dark blue precipitate which was filtered, washed with methanol, and dried *in vacuo*.

Yield: 120 mg (17%); soluble in CH_2Cl_2, $CHCl_3$, *THF*, and *DMF*; UV/Vis ($CHCl_3$): $\lambda_{max} = 708$ (48300), 676 (13090), 654 (11940), 616 (26600), 346 (34480) nm (ε); IR (KBr): $\bar{\nu} = 3280$ (NH), 3050 (Ar-CH), 3000-2900 (aliph. CH), 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.13-7.39 (m, 12 Ar-H), 3.88 (d, 2 SCH_2), 1.92-1.25 (m, 8 CH_2), 0.96 (t, 2 CH_3), -4.0 (broad s, 2 NH) ppm.

Palladium dichloride complex of 22,23-di(hexylthio)-μ-27H,29H-tribenzo[b,g,l]porphyrazine (**4**; $C_{40}H_{40}N_8S_2PdCl_2$)

3 (696 mg, 1 mmol) was refluxed with 383 mg $PdCl_2(C_6H_5CN)_2$ (1 mmol) in 20 cm^3 $CHCl_3$ under N_2 for 12 h. The mixture was filtered, and the filtrate was evaporated to dryness. When the residue was treated with *n*-hexane, the crude product was precipitated. It was filtered, washed first with *n*-hexane and then with methanol, and dried *in vacuo*.

Yield: 200 mg (23%); soluble in $CHCl_3$, CH_2Cl_2, and *THF*; UV/Vis ($CHCl_3$): $\lambda_{max} = 703$ (15560), 684 (20120), 637 (12920), 579 (11800), 344 (22160) nm (ε); IR (KBr): $\bar{\nu} = 3280$ (NH), 3050 (Ar-CH), 3000-2900 (aliph. CH), 1250 cm^{-1}; ^{1}H NMR ($CDCl_3$, δ, 250 MHz): 8.87-7.97 (m, 12 Ar-H), 3.74 (s, 2 SCH_2), 1.56-1.01 (m, 8 CH_2), 0.88 (t, 2 CH_3), -1.3 (broad s, 2 NH) ppm.

Acknowledgements

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