Mono-, Di-, and Trimetallic Palladium(II) Porphyrin Trimers with Etheno-bridges

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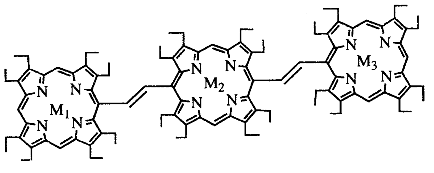
Mono-, di-, and trimetallic Pd(II) complexes of the etheno-bridge porphyrin trimer **1** were prepared. It was found that the metalation of **1** first occurred in the inner porphyrin ring. The trimetallic Pd(II) trimer **6** exhibited splitting of the Soret band and complete disappearance of the weak bands ranging from 600 to 1000 nm unlike the corresponding free-base and Ni(II) porphyrin trimers.

In connection with an intensive study of the electronic properties for the linear porphyrin oligomers,[1] we previously reported the synthesis of the etheno-bridge porphyrin trimer **1** and showed its peculiar electronic features, from which it was proved that the electron-releasing ability of the trimer **1** was remarkably enhanced as compared with that of octaethylporphyrin (**OEP**).[2] In continuation of our investigations on the electronic properties of the etheno-bridge porphyrin trimer **1**, the mono-, di-, and trimetallic Pd(II) complexes were prepared. We describe their metalation and spectral features, along with comparison of electronic spectral behavior between Pd(II) and Ni(II) metalloporphyrins both of which are well known to be in the group of the hypso type.[3]

Metalation of the free-base porphyrin trimer **1** was carried out using one molar equivalent of Pd(II) acetate ($Pd(OAc)_2$) in a mixture of dichloromethane and methanol (5:1).[3] Chromatography of the reaction products on SiO_2 with a mixture of hexane and dichloromethane (95:5 ~ 0:100) gave the Pd(II) complexes of trimetalated (**6**; 20% based on $Pd(OAc)_2$), dimetalated (**4**; 40%), and monometalated (**3**; 22%) porphyrin trimers in order of the eluted fractions, together with some amount of the starting material **1** (ca. 10%) from the last fractions.[4] Their structures were unambiguously determined by means of MS and ^1H NMR spectra (see below). In the metalation of **1**, neither the monometallic isomer **2** for **3** nor the symmetrically dimetalated isomer **5** for **4** was formed at all, against expectation that in the latter case the dimetallic isomer **5** would be formed preferably, since the electrostatic repulsion between two Pd(II) cations in **5** is smaller than that in the unsymmetrical isomer **4**. These results indicate that the metalation of the free-base trimer **1** first takes place in the inner porphyrin ring exclusively, apparently showing that the NH protons of the inner ring are more acidic than those of the outer ones,[3c] and that the metalated ring in turn facilitates the metalation of the neighbour free-base ring.



1 : $M_1 = M_2 = M_3 = H_2$
2 : $M_1 = Pd,\ M_2 = M_3 = H_2$
3 : $M_2 = Pd,\ M_1 = M_3 = H_2$
4 : $M_1 = M_2 = Pd,\ M_3 = H_2$
5 : $M_1 = M_3 = Pd,\ M_2 = H_2$
6 : $M_1 = M_2 = M_3 = Pd$

Chemical shifts of the selected protons of the metalated and related porphyrins are given in Table. The meso and etheno-bridge protons for both mono- (**3**) and trimetallic (**6**) trimers exhibited the same signal patterns as those for the free-base **1**, indicating that both of them essentially possess the C_2 symmetry, with the etheno-bridges in a trans configuration.[2] On the other hand, the dimetallic trimer (**4**) gave the relatively complex spectrum which indicates the collapse of the molecular symmetry, exhibiting five singlet signals due to the meso protons and two sets of AB doublet signals due to the trans etheno-bridge ones with coupling constants of ca. 15 Hz. In addition to these spectral appearances, from the fact that the metalation of the free-base porphyrin ring should be accompanied by the loss of NH protons, disappearance of the lowfield NH signal prior to the upfield one in the free-base trimer **1** clearly supports that the first metalation of **1** occurred in the inner porphyrin ring to afford **3**, as mentioned above.

Little difference in chemical shift of the peripheral meso and

Table 1. The ^1H NMR chemical shifts of meso, etheno-bridge, and NH protons of the porphyrin derivatives (400 MHz, $CDCl_3$, δ at 22° C)

	meso-H	etheno-bridge-H	NH
OEP	10.10 (4H)		- 3.76 (2H)
Pd - OEP	10.12 (4H)		
1[a] (Free-base Trimer)	10.07 (4H), 9.89 (2H), 9.68 (2H)	8.57 (2H), 8.48 (2H)	- 1.25 (2H) - 2.54 (4H)
3 (Monometallic **Pd** Trimer)	10.12 (4H), 9.99 (2H), 9.98 (2H)	8.48 (2H), 8.12 (2H)	- 2.88 (4H)
4 (Dimetallic **Pd** Trimer)	10.12 (2H), 10.09 (2H), 10.05 (1H) 9.99 (1H), 9.98 (2H)	8.47 (1H), 8.16 (1H) 8.10 (1H), 8.05 (1H)	- 2.93 (2H)
6 (Trimetallic **Pd** Trimer)	10.08 (4H), 10.04 (2H), 9.99 (2H)	8.16 (2H), 8.03 (2H)	

[a] See Ref. 2.

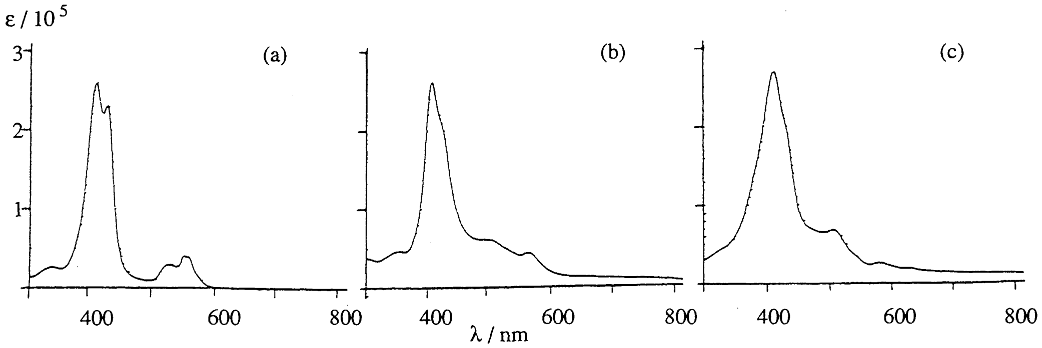


Figure 1. Electronic absorption spectra of (a) **6**, (b) the trimetallic Ni(II) trimer of **1**, and (c) the free-base **1** in $CHCl_3$.

ethyl protons between **OEP** and **Pd-OEP** indicates that an incorporation of Pd(II) ion essentially does not affect the ring current of porphyrin ring.[3a, 5] The high similarity in chemical shift of the meso-H was also observed between the free-base (**1**) and the Pd(II) trimer (**6**), though a very little lowfield shift was observed for **6**. All etheno-bridge-Hs of the metallic trimer **6**, however, shifted to the high field by more than 0.4 ppm from those of the free-base **1**. The trend of upfield shift for the etheno-bridge-H adjacent to the metalated ring is also true for the molecules which have both free-base and metalated rings, like the trimers **3** and **4**. In the dimetallic trimer **4**, for example, three of four etheno-bridge-Hs appeared at the high field region by 0.3-0.4 ppm from the last one. This may supply a crucial information on the structural assignment of the metalated ring in this type of etheno-bridge porphyrin oligomers. In addition, an incorporation of Pd(II) ion induces the upfield shift of NH in the neighbour free-base ring, exhibiting the high field resonances with an increase of the metalated ring; **1** << **3** < **4**. These results obtained by the chemical shift changes of those protons between before and after the metalation may indicate that an incorporation of Pd(II) ion causes the conformational changes about the etheno-bridges and thus changes the shielding scope[1a] arising from the diamagnetic ring current of the π-electronic system in **1**.

In the electronic absorption spectra, both monometallic (**3**)[4] and dimetallic (**4**)[4] trimers showed the high similarity in not only absorption curve with a long tail up to 900-1000 nm but also absorption maxima to the corresponding trimetallic Ni(II) trimer[2] (Figure (**b**)) and the free-base trimer **1** (Figure (**c**)), though the Soret band sharpened slightly in the metalloporphyrins. The trimetallic trimer **6** (Figure (**a**)), however, exhibited the distinctly different absorption spectrum from that of the free-base **1**; split of Soret band (409 and 427 nm), hypsochromic shift of Q bands (530, 554, and 561 nm), and complete disappearance of the weak absorption bands over 400 nm between 600 and 1000 nm. It is worthy of note that a considerable similarity in the electronic absorption spectrum is observed between **Ni**-[3a] and **Pd-OEP**[3b] which are both d^8-metalloporphyrins classified as the group of the hypso type,[3c] while a distinctive difference between the trimetallic **Ni**-trimer and the trimetallic **Pd**-trimer. Although it is premature to deduce the decisive conclusion for these results, it is indicated that the electronic interaction of the porphyrin ring system with the $4d^8$-Pd(II) ion[3] is extremely enhanced in this type of etheno-bridge porphyrin trimer as compared with that with the $3d^8$-Ni(II) ion.

Further examinations of their properties for elucidation of the electronic interaction in the trimeric metalloporphyrin system are underway.

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References and Notes

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3 a) J. W. Buchler and L. Puppe, *Liebigs Ann. Chem.*, **1970**, 142. b) J. W. Buchler and L. Puppe, *Liebigs Ann. Chem.*, **1974**, 1046. c) J. W. Buchler, In *The Porphyrins*, ed. D. Dolphin, Academic Press, London (1978), Vol. I.

4 All new compounds **3**, **4**, and **6** gave satisfactory analytical and spectral data. Selected electronic absorption spectral data of **3** and **4** are as follows.
3 (λ_{max}/nm (ε) in $CHCl_3$): 330 (sh, 34000), 375 (sh, 95000), 416 (271000), 426 (sh, 255000), 509 (34500), 541 (28000), 577 (24600), 633 (7600), and the very weak bands up to 1000 nm. **4**: 330 (sh, 32000), 412 (288000), 427 (sh, 258000), 517 (sh, 27500), 540 (29500), 553 (32500), 562 (sh, 29500), 578 (sh, 21000), 633 (4250), and the very weak bands up to 900 nm.

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