Monatshefte für Chemie 134, 1555–1560 (2003)
DOI 10.1007/s00706-003-0074-5

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Synthesis and Characterisation of Unsymmetrical Porphyrazines Containing Bis(hydroxyethylthio) Substituents

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Received May 14, 2003; accepted May 19, 2003
Published online September 18, 2003 © Springer-Verlag 2003

Summary. Unsymmetrical porphyrazines bearing a single peripheral bis(hydroxyethylthio) moiety were synthesised by mixed condensation of bis(2-hydroxyethylthio)maleonitrile and phthalonitrile. Complexation of the thioether groups of metal-free porphyrazine with $PdCl_2$ further lowered the intensity of the Q-band absorption of the porphyrazine core. The new compounds were characterised by elemental analyses, IR, ^1H NMR, UV-Vis, and mass spectra.

Keywords. Porphyrazine; Phthalocyanine; Palladium; Complex.

Introduction

Phthalocyanines and porphyrins have received considerable attention due to interesting applications [1, 2]. In addition to their traditional applications as dyes and pigments, the special characteristics of phthalocyanines make them suitable as charge carriers in electrophotography [3] and as the dye component in optical data storage systems [4]. Furthermore, their properties have been identified as having potential for exploitation in a number of other fields including gas sensing [5], photovoltaic cells [6], optical limiting [7], and photodynamic therapy of cancer [8]. The unique properties of porphyrins lead to their importance in the development of molecular optoelectronic gates and switches [9], photo-inducible energy [10], semiconductors [11], and enzyme models [12].

In comparison to phthalocyanines and porphyrins, porphyrazines have been studied less frequently for a long period. Starting with the general high-yield route to octakis(alkylthio)porphyrazine by *Hoffmann* [13], an extensive series of derivatives with physical and chemical properties comparable to those of phthalocyanines have been reported [14–17].

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In contrast to the symmetrical porphyrazines, which are obtained directly by cyclotetramerization of an unsaturated dinitrile, unsymmetrical ones require the development of new methods of synthesis and separation. Unsymmetrically substituted derivatives functionalized with heteroatoms can bind additional metal ions, have the potential to exhibit novel magnetic and electronic properties, and serve as building blocks in the assembly of higher order polymetallic arrays. Also the presence of soft S donor atoms play an important role in affecting the solid state interactions [18–20].

Our previous papers have described a series of symmetric and unsymmetric phthalocyanines carrying various substitutents, *e.g.* triaza or dioxadiaza macrocycles, or alkylthio groups on the periphery [21–25]. It has been shown that the peripheral substituents enhance the solubility in common organic solvents and provide donor sites for binding transition metal ions leading to heteromultinuclear complexes.

In the present paper we report the synthesis of unsymmetrical porphyrazines having a single peripheral bis(hydroxyethylthio) moiety. Also a palladium(II) complex of the metal-free porphyrazine was prepared.

Results and Discussion

Unsymmetrical porphyrazines can be synthesized by co-cyclizing two different precursors (A and B). When stoichiometric amounts are used, a mixture of all six possible porphyrazine products is obtained naturally, and separation of the desired singly substituted AB_3 product by column chromatographic techniques can be very difficult. When one of the precursors, *e.g.* B, is present in excess, only two products are obtained, the fully symmetric B_4 porphyrazine and the desired AB_3 porphyrazine.

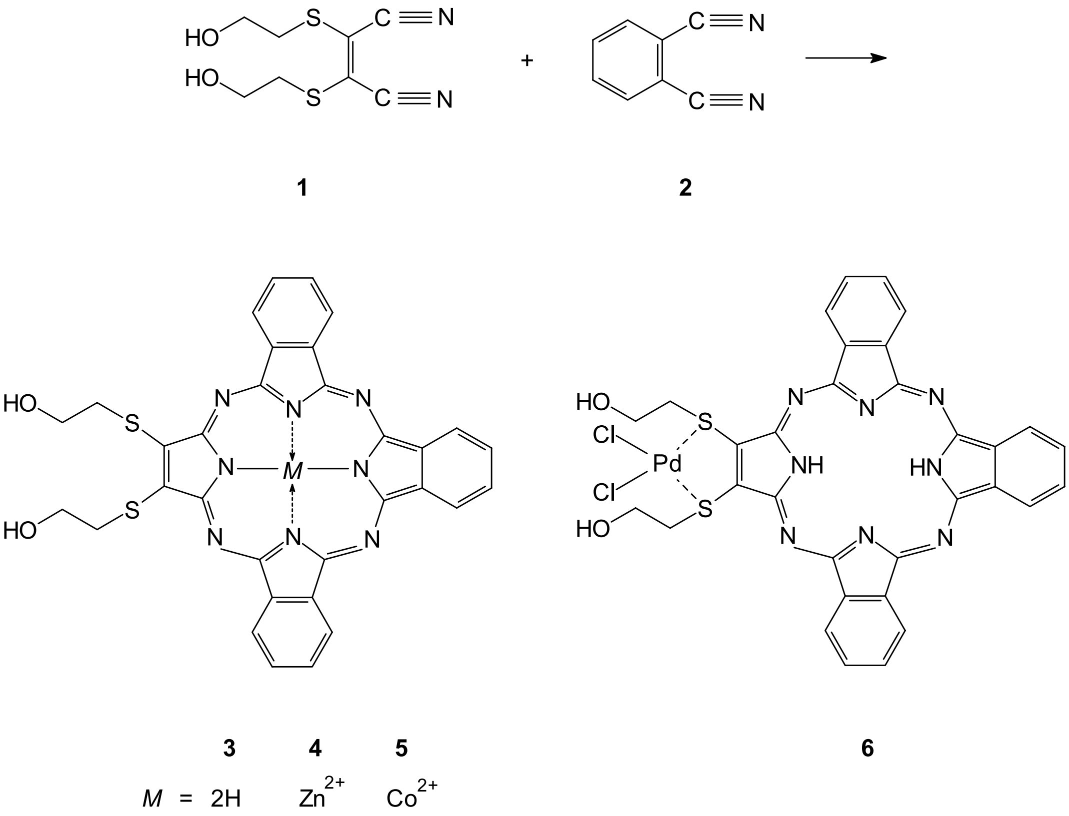
In this work, unsymmetrical magnesium porphyrazine was prepared by the reaction of bis(2-hydroxyethylthio)maleonitrile (**1**) [26] with phthalonitrile (**2**) in 1:25 ratio in a suspension of magnesium butoxide in refluxing butanol. The reason for using one of the reagents in large excess was to minimize the formation of cross tetramerization products and to promote the formation of the 3:1 product and phthalocyanine.

Demetalization of these products by trifluoroacetic acid produced metal-free phthalocyanine and unsymmetrical metal-free porphyrazine **3**. Metal-free phthalocyanine is hardly soluble in most organic solvents, whereas **3** is soluble with the proper selection of a thioether protecting group. The purple product **3** was isolated from the reaction mixture by *Soxhlet* extraction with *THF*.

Remetallation of the porphyrazine core with Zn(II) or Co(II) proceeds by treatment of the free porphyrazine **3** with a small excess of the appropriate metal acetate to produce **4** and **5**. In contrast to the hexlythio analog, the solubility of the unsymmetrical porphyrazines **3**–**5** is very low.

The reaction of the palladium(II) ion with the thioether groups of **3** gave a product having a five membered chelate ring. The solubility of this four coordinate palladium complex **6** is even lower than that of the parent porphyrazine **3**.

Elemental analysis results, ^{1}H NMR, IR, UV-Vis, and mass spectral data for all new products were consistent with the assigned formulae. In the IR spectrum of **3**,



Scheme 1

the disappearance of the intense C≡N stretching vibrations of precursors **1** and **2** can be taken as a clear evidence for tetrapyrrole formation. Also, characteristic NH stretching vibrations of the inner core and CH stretching vibrations of aliphatic groups in **3** were observed at $\bar{\nu} = 3285$ and 2930–2800 cm^{-1}. The IR spectra of the porphyrazine complexes **4** and **5** were very similar to **3**, with the exception of a NH stretching band at $\bar{\nu} = 3285\,cm^{-1}$.

The ^{1}H NMR spectrum of **3** exhibited the aromatic protons around $\delta = 8.32$ and 7.24 ppm as multiplet and the OCH_2 and SCH_2 protons of the hydroxyethylthio moiety at $\delta = 3.98$ and 3.60 ppm as triplet. The OH group of **3** was observed at $\delta = 4.81$ ppm. Inner core –NH protons of metal-free porphyrazine **3** appeared as a deuterium exchangeable broad signal at $\delta = -2.42$ ppm indicating the 18π electron system of the planar molecule. These values are comparable with those for other substituted porphyrazines [26–28]. In addition to the elemental analysis results the mass spectral analysis is critical in determining the ratio of the two precursors as 3:1 after the cyclotetramerization reaction. The M^+ ion peak at $m/z = 616$ (EI) for **3** provides strong evidence for a 3:1 condensation of the precursors.

Phthalocyanines and porphyrazines display similar and characteristic absorption spectra. Porphyrazines, like phthalocyanines, exhibit two main bands, a *Soret* (B band) between $\lambda = 330$–375 nm and another one (Q band) beyond $\lambda = 650$ nm. The optical spectra of unsymmetrical metallo porphyrazines **4** and **5** exhibit an intense absorption in the *Soret* region at $\lambda = 346$ and 326 nm and a broad Q band at

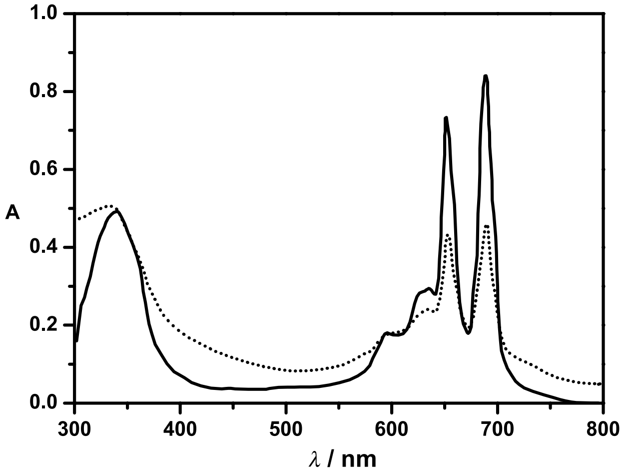


Fig. 1. UV-Vis of unsymmetrical metal-free porphyrazine **3** (——) and its $PdCl_2$ complex **6** (......)

$\lambda = 666$ and 656 nm, respectively. The spectrum of the metal-free porphyrazine **3** is quite similar, but with a split Q band having Q_x and Q_y absorbances at $\lambda = 653$ and 690 nm. The electronic spectra of **3** and its Pd complex **6** are shown in Fig. 1. After complexation a distinct decrease in the Q band has occurred. This can be interpreted as a lowering of the electron density in the tetrapyrrole unit after binding a cationic species directly to the thioether donors on the periphery.

Experimental

IR spectra were recorded on a Mattison 1000 FTIR spectrometer (KBr). 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 (C, H, N) were carried out by the analysis laboratory of the Tübitak Marmara Research Center. The results were in favourable agreement with the calculated values. Compound **1** was synthesised according to Ref. [26].

22,23-Di(2-hydroxyethylthio)-μ-27H,29H-tribenzo[b,g,l]porphyrazine (**3**, $C_{32}H_{24}N_8S_2O_2$)

A suspension of 0.312 g of Mg powder (13 mmol) in 50 cm^3 of *n*-butanol was refluxed overnight after addition of a few crystals of I_2 to initiate the reaction. To this mixture, 0.230 g of bis(2-hyroxyethylthio)maleonitrile (1 mmol) and 3.2 g of phthalonitrile (25 mmol) were added. The reaction mixture was kept at reflux under N_2 for 12 h. After the hot mixture was filtered, the precipitate was refluxed with acetone, methanol, and filtered off. The crude magnesium porphyrazine was dissolved in 5 cm^3 of trifluoroacetic acid and stirred at room temperature for 3 h. The solution was added dropwise into ice/H_2O in order to precipitate the product and then neutralised with aqueous NH_3 (10%). The resulting precipitate was filtered off and washed first with H_2O, ethanol, and dried *in vacuo*. The solid product was extracted with *THF* in a *Soxhlet* for 24 h. After evaporation of the solvent a pure product was obtained by washing the residue with methanol and diethyl ether. Yield: 0.073 g (12%); IR (KBr): $\bar{\nu} = 3330$ (OH), 3285 (NH), 2930–2800 (alkyl CH), 1042 (CO) cm^{-1}; ^{1}H NMR (*DMSO*-d$_6$): $\delta = -2.42$ (broad s, NH), 3.60 (t, $J = 6.82$ Hz, $4SCH_2$), 3.98 (t, $J = 6.89$ Hz, $4OCH_2$), 4.81 (s, 2OH), 8.32–7.24 (m, 12Ar-H) ppm; UV-Vis (*THF*): $\lambda(\lg \varepsilon) = 690$ (4.63), 653 (4.57), 339 (4.39) nm.

22,23-Di(2-hydroxyethylthio)tribenzo[b,g,l]porphyrazinatozinc(II) (**4**, $C_{32}H_{22}N_8S_2O_2Zn$)

To a solution of 0.125 g of **3** (0.2 mmol) in 20 cm^3 of *THF* a solution of 73 mg of $Zn(CH_3COO)_2$ (0.4 mmol) in 10 cm^3 of absolute ethanol was added under N_2. The mixture was heated under reflux for 18 h. The crude product was filtered and washed with H_2O, methanol, and ethanol. The blueish green product was dried under vacuum. Yield: 0.120 g (88%); IR (KBr): $\bar{\nu} = 3310$ (OH), 2953–2876 (CH), 1038 (CO) cm^{-1}; UV-Vis (*THF*): $\lambda(\lg \varepsilon) = 666$ (4.84), 346 (4.42) nm.

22,23-Di(2-hydroxyethylthio)tribenzo[b,g,l]porphyrazinatocobalt(II) (**5**, $C_{32}H_{22}N_8S_2O_2Co$)

Compound **5** was prepared according to the same procedure as described for **4** by starting from 0.125 g of **3** (0.2 mmol) and 71 mg of $Co(CH_3COO)_2$ (0.4 mmol). Yield: 0.114 g (85%); IR (KBr): $\bar{\nu} = 3300$ (OH), 2960−2870 (CH), 1060 (CO) cm^{-1}; UV-Vis (*THF*): λ (lg ε) = 656 (4.41), 326 (4.30) nm.

22,23-Di(2-hydroxyethylthio)-μ-27H,29H-tribenzo[b,g,l]porphyrazinatopalladium(II) chloride
(**6**, $C_{32}H_{24}N_8S_2O_2PdCl_2$)

Compound **3** (0.250 g, 0.4 mmol) was refluxed in 10 cm^3 of *THF* for 12 h under N_2 in the presence of 0.153 g of $PdCl_2(C_6H_5CN)_2$ (0.4 mmol). The dark blue precipitate was filtered off, washed with methanol, and dried *in vacuo*. Yield: 0.079 g (25%); IR (KBr): $\bar{\nu} = 3330$ (OH), 3285 (NH), 2930−2800 (CH), 1042 (CO) cm^{-1}; UV-Vis (*THF*): λ (log ε) = 690 (4.37), 654 (4.34), 331 (4.41) nm.

Acknowledgement

This work was supported by the Research Fund of the Technical University of Istanbul.

References

[1] Leznoff CC, Lever ABP (eds) (1989–1993) Phthalocyanines Properties and Applications, VCH, Weinheim

[2] McKeown NB (1998) Phthalocyanine Materials: Synthesis, Structure and Function. Cambridge University Press, Cambridge

[3] Gregory P (2000) J Porphyrin Phthalocyanin **4**: 432

[4] Birkett D (2000) Chem Ind 178

[5] Ding X, Zhu H, Xu HJ, Jiang DP (2002) J Porphyrin Phthalocyanin **6**: 366

[6] Eichhorn H (2000) J Porphyrin Phthalocyanin **4**: 88

[7] Shirk JS, Pong RGS, Flom SR, Hechmann H, Hanach M (2000) J Phys Chem **104**: 1438

[8] a) Allen CM, Langlois R, Sharman WM, LaMadeleine C, van Lier JE (2002) Photochem Photobiol **76**: 208; b) Ali H, van Lier JE (1999) Chem Rev **99**: 2379

[9] Wagner RW, Lindsey JS, Seth J, Pallnaippan V, Bocian DJ (1996) J Am Chem Soc **118**: 3996

[10] Sessler JL, Wang B, Harriman A (1995) J Am Chem Soc **117**: 704

[11] Simon J, Andre JJ (1985) Molecular Semiconductors, Springer, Berlin

[12] Collman JP, Fu L, Herrmann PC, Zhang X (1997) Science **275**: 949

[13] Anderson K, Anderson M, Anderson OP, Baum S, Baumann TF, Beall LS, Broderick WE, Cook AS, Eichhorn DM, Goldberg D, Hope H, Jarrell W, Lange SJ, McCubbin QJ, Mani NS, Miller T, Montalban AG, Rodriguez-Morgade MS, Lee S, Nie H, Olmstead MM, Sabat M, Sibert JW, Stern C, White AJP, Williams DBG, Williams DJ, Barrett AGM, Hoffman BM (1998) J Heterocycl Chem **35**: 1013

[14] Mitnel F, FitzGerald S, Beeby A, Faust R (2003) Chem Eur J **9**: 1233

[15] Angeloni S, Ercolani C (2000) J Porphyrin Phthalocyanin **4**: 474

[16] Stuzhin PA, Bauer EM, Ercolani C (1998) Inorg Chem **37**: 1533

[17] Bakboord JV, Cook MJ, Hamuryudan E (2000) J Porphyrin Phthalocyanin **4**: 510

[18] Lange SJ, Nie H, Stern CL, Barrett AGM, Hoffman BM (1998) Inorg Chem **37**: 6435

[19] Sakellariou EG, Montalban AG, Meunier HG, Ostler RB, Rumbbs G, Barrett AGM, Hoffmann BM (2000) J Photochem Photobiol A: Chem **136**: 185

[20] Silbert JW, Baumann TF, Williams DJ, White AJP, Barrett AGM, Hoffmann BM (1996) J Am Chem Soc **118**: 10487

[21] Bayır ZA, Hamuryudan E, Bekaroğlu Ö (1999) J Chem Res (S); 702; (M) 1999: 3030

[22] Hamuryudan E, Bayır ZA, Bekaroğlu Ö (1999) Dyes and Pigments **43**: 77

[23] Gürsoy S, Bayır ZA, Hamuryudan E, Bekaroğlu Ö (2000) Monatsh Chem **131**: 287

[24] Bayır ZA, Hamuryudan E, Gürek AG, Bekaroğlu Ö (1997) J Porphyrin Phthalocyanin **1**: 349

[25] Bayır ZA, Merey Ş, Hamuryudan E (2003) Monatsh Chem **134**: 1027

[26] Akkuş H, Gül A (2001) Transition Met Chem **26**: 689

[27] Sesalan BŞ, Gül A (2000) Monatsh Chem **131**: 1191

[28] Sağlam Ö, Gül A (2001) Polyhedron **20**: 269