Much attention has focused in recent years on porphyrins bearing sterically demanding substituents with nonplanar conformations. It has been established that different macrocycle conformations result in altered physicochemical properties of the porphyrin cofactors in vivo and technical applications of this concept have been described as well [1–4]. Of special interest are 5,10,15,20-tetraalkylporphyrins with a ruffled conformation or 2,3,7,8,12,13,17,18-octaalkylaryl-5,10,15,20-tetraarylporphyrins with a saddle conformation [5–8].

In order to elucidate the mutual interrelationship between macrocycle conformation and properties it is necessary to prepare series of porphyrins with gradually altered distortion modes for detailed physicochemical studies [9]. While numerous 5,10,15,20-tetraalkylporphyrins have been prepared these are either only moderately distorted (e.g. with isopropyl) or highly nonplanar (with t-butyl residues) and prone to side reactions [5–7,10,11]. The only alkylporphyrins with an intermediate degree of ruffling were 5,10,15,20-tetracyclohexylporphyrin [12]. After the second purification step, using neutral alumina, only one product was observed, presumably due to interconversion of the different atropisomers into the most stable form. Utilizing standard metallation techniques various metal complexes of the free base porphyrin are accessible and the complexes 2–4 were prepared in the hope to obtain crystals suitable for X-ray crystallography. Unfortunately, only the Co(II) complex 4 gave crystals of marginal size suitable for analysis (see below). Despite various syntheses of the Ni(II) complex 3 we were unable to obtain a meaningful 1H NMR spectrum; always formation of a mixture of atropisomers was observed. In no case we observed side reactions resulting in disruption of the aromatic system as have been described for 5,10,15,20-tetra(tert-butyl)porphyrin [6,10]. With access to the title compound, a relatively ruffled tetraalkylporphyrin is now in hand that is amenable for further synthetic modifications without the problems associated with tetra(t-butyl)porphyrin.

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On the basis of the spectroscopic data in methylene chloride the free base porphyrin 1 ($\lambda_{Soret} = 433$ nm) takes an intermediate position between tetracyclohexylporphyrin ($\lambda_{Soret} = 422$ nm) and tetra($\tau$-butyl)porphyrin ($\lambda_{Soret} = 446$ nm) with regard to its conformational distortion. For comparison, the planar 5,10,15,20-tetra($\tau$-butyl)porphyrin exhibits a $\lambda_{Soret}$ of 416 nm [10]. The bathochromic shift of the absorption maxima is known to directly correlate with the degree of conformational distortion [8a]. The situation is not as clear for the related metal complexes. Both the Ni(II) and Co(II) complexes of 1 show a small hypsochromic shift compared to the respective 5,10,15,20-tetra-cyclohexylporphyrin metal complexes. Presumably, the metal complexes have a large degree of conformational flexibility.

A similar observation can be made on the basis of the crystal structure of 4. The cobalt(II) complex crystallized as the pentacoordinated complex with a methanol serving as axial ligand to the cobalt center (Fig. 1). Selected structural parameters are compiled in Table I. The macrocycle conformation is characterized by a typical ruffled distortion mode with significant out-of-plane displacements of the meso carbon positions ($\Delta C_m = 0.55$ Å) and twisting of the pyrrole rings about the C$_b$-C$_b$ axis. The degree of nonplanarity is similar to that found in [5,10,15,20-tetraphenylporphyrinato]cobalt(II) [17a]. Thus, contrary to the situation found for the free base, the solid state structure of 4 gives no evidence for significant steric strain in this compound. In the absence of any related cobalt(II) tetraalkylporphyrin structures for comparison we can only surmise that metal complexes of the title compound have a high degree of conformational flexibility whose conformation is easily affected by other factors, for example packing forces. The present structure shows some short intermolecular contacts, e.g. between aryl ring hydrogen atoms and cobalt centers (2.7–3 Å), and the axial methanol molecule forms a hydrogen bond to a methanol of solvation (O1S-O2S = 2.803 Å).

The overall structural parameters are close to those of other cobalt(II) porphyrins [18]. The Co-N bonds are significantly shorter than in the planar [2,3,7,8,12,13,17,18-octaethylporphyrinato]cobalt(II) [1.971(6) Å] [17b] and slightly longer than in [5,10,15,20-tetraphenylporphyrinato]cobalt(II) [1.949(3) Å] [17a]. Compared to highly saddle distorted cobalt porphyrins the Co-N bond lengths in 4 are slightly shorter than in [2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitro-...
Table I. Structural and geometrical parameters for 4.

<table>
<thead>
<tr>
<th>Bond lengths [Å]</th>
<th>Co-Oa</th>
<th>2.230(5)</th>
</tr>
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<tbody>
<tr>
<td>Co-N</td>
<td>1.954(5)</td>
<td></td>
</tr>
<tr>
<td>N-Ca</td>
<td>1.385(8)</td>
<td></td>
</tr>
<tr>
<td>Ca-Cb</td>
<td>1.439(9)</td>
<td></td>
</tr>
<tr>
<td>Ca-Cm</td>
<td>1.392(9)</td>
<td></td>
</tr>
<tr>
<td>Cb-Cb</td>
<td>1.338(9)</td>
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</table>

<table>
<thead>
<tr>
<th>Bond angles [deg]</th>
<th>N-Co-N opp</th>
<th>174.6(2)</th>
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<tbody>
<tr>
<td>N-Co-N adj</td>
<td>89.9(2)</td>
<td></td>
</tr>
<tr>
<td>Co-N-Ca</td>
<td>126.9(4)</td>
<td></td>
</tr>
<tr>
<td>N-Ca-Cm</td>
<td>109.3(5)</td>
<td></td>
</tr>
<tr>
<td>Ca-Cm-Ca</td>
<td>106.1(5)</td>
<td></td>
</tr>
<tr>
<td>Ca-Cm-Cb</td>
<td>121.9(6)</td>
<td></td>
</tr>
<tr>
<td>Ca-Cb-Cb</td>
<td>107.6(6)</td>
<td></td>
</tr>
<tr>
<td>Cb-Cb-Cb</td>
<td>125.1(6)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structural parameters [Å]</th>
<th>∆24 a</th>
<th>0.268</th>
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<tbody>
<tr>
<td>∆Co b</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>∆N c</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>∆Cm d</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>∆Cb e</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>∆Cb f</td>
<td>0.20</td>
<td></td>
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</table>

a Average deviation of the macrocycle atoms from their least squares plane; b average deviation from the 4N-plane.

Porphyridinato)cobalt(II) [1.964(5) Å] [19a] and longer than in [2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)cobalt(II) [1.929(3) Å] [19b]. For comparison, the only related tetraalkylporphyrin structure, (5,10,15,20-tetraheptafluoropropyl)porphyrinato)cobalt(II), albeit with a saddle distorted macrocycle, exhibits an average Co-N bond length of 1.936 Å [19c].

**Experimental**

General experimental and instrumental techniques used were as described before [20].

**Synthesis of 5,10,15,20-tetakis(diphenylmethyl)porphyrinato)cobalt(II) (1)**

Pyrrole (1.4 ml, 0.02 mol) and 0.02 mol diphenylacetaldehyde (2.5 ml, 3.96 g) were dissolved under an Ar atmosphere in 21 absolute methylene chloride. After dropwise addition of 0.02 mol TFA (1.5 ml) the reaction mixture was stirred for 12 h at room temperature. This was followed by addition of 0.016 mol DDQ (3.36 g) and stirring for an additional hour. The crude reaction mixture was filtered through neutral alumina (Brockmann grade III) and chromatographed on alumina (Brockmann grade III eluting with CH2Cl2/n-hexane (2:1, v/v). Recrystallization from CH2Cl2/CH2OH yielded 779 mg (0.81 mmol, 16%) dark-purple crystals; m.p. 210–215 °C. – UV/vis (CH2Cl2): λmax (lg ε) = 433 nm (5.26), 530 (4.08), 565 (3.60), 607 (3.55), 665 (3.24). – 1H NMR (250 MHz, CDCl3, TMS): δ = -1.60 (s, 2H, NH), 7.16–7.28 (m, 24H, H0-porphyril), 7.41–7.44 (d, J = 6.8 Hz, 16H, H0-porphyril), 8.11 (s, 4H, CH(C6H5)2). 8.74 (s, 8H, Hβ-pyrrole). – MS (40 eV); m/z (%): 974 (100) [M+], 808 (77) [M+ – C13H11] 642 (23) [M+ – 2x C13H11].

C72H54N4Zn.CH2OH (1029.428)

Calcd C 84.02 H 5.29 N 5.44%

Found C 84.31 H 5.47 N 5.04%

**Synthesis of 5,10,15,20-tetakis(diphenylmethyl)porphyrinato)zinc(II) (2)**

The free base 1 (0.1 mmol, 100 mg) was dissolved in 50 ml CH2Cl2 and treated under stirring with 250 mg ZnO and 3 drops of TFA. After 10 minutes a color change from green to purple was observed. The crude mixture was filtered through silica gel and recrystallized from CH2Cl2/CH3OH. Yield: 60 mg (0.058 mmol, 57%) red-purple crystals; m.p. 230–232 °C. – UV/vis (CH2Cl2): Amax (lg ε) = 434 nm (5.8), 565 (4.66). – 1H NMR (250 MHz, CDCl3, TMS): δ = 7.14–7.26 (m, 24H, H0-porphyril), 7.41–7.44 (d, J = 7.0 Hz, 16H, H0-porphyril), 8.23 (s, 8H, CH(C6H5)2), 9.10 (s, 8H, Hβ-pyrrole). – MS (40 eV); m/z (%): 1036 (100) [M+], 870 (7) [M+ – C13H11].

C72H52N4Zn • CH3OH (1070.66)

Calcd C 81.89 H 5.27 N 5.23%

Found C 81.67 H 5.27 N 5.20%

**Synthesis of 5,10,15,20-tetakis(diphenylmethyl)porphyrinato)nickel(II) (3)**

0.1 mmol (100 mg) of the free base 1 were dissolved in 10 ml DMF. Nickel(II) acetate (100 mg) was added and the mixture heated under reflux for 30 minutes. After addition of 100 ml cold water the precipitate was filtered off, washed with warm water, and chromatographed on silica gel (CH2Cl2/n-hexane, 1:1, v/v). Yield: 50 mg (0.048 mmol, 48%) dark-red crystals from CH2Cl2/
500 mg of the free base 1 were dissolved in 250 ml CH2Cl2, treated with 5 ml of a saturated solution of cobalt acetate and heated under reflux for 10 h. The mixture was washed with water and purified on silica gel (CH2Cl2/n-hexane, 1:1, v/v). Yield: 70 mg (0.066 mmol, 13%) purple crystals from CH2Cl2/CH3OH; m.p. 250–253 °C. - UV/vis (CH2Cl2): A max (lg e) = 422 nm (5.10), 560 (4.02). - MS (40 eV); m/z (%): 1031 (3) [M+], 865 (11) [M+ – C13H10], 699 (18) [M+ – 2x C13H10].

C72H52N4Co
Calcd 1031.3524
Found 1031.3525 (HRMS).

Crystal structure determination of 4

X-ray quality crystals were grown by liquid diffusion from CH2Cl2/CH3OH. The crystals were removed from solution and covered with a layer of Paraton N®. A suitable crystal was selected, attached to a glass fiber and immediately placed into the low-temperature nitrogen stream as described by Hope [21]. Intensity data were collected at 94 K with a Siemens SMART system complete with 3-circle goniometer and CCD detector utilizing Mo-Kα radiation (λ = 0.71073 Å). The data collection nominally covered a hemisphere of reciprocal space. No decay was observed during the data collection. An absorption correction was applied using the program SADABS [22], while extinction effects were disregarded. The structure of 3e was solved via a Patterson synthesis followed by structure expansion [23a]. Refinements were carried out by full-matrix least-squares on F2 using the program SHELXL-93 [23b]. Hydrogen atoms were included at calculated positions using a riding model. All nonhydrogen atoms were refined with anisotropic thermal parameters. Although the resolution of the structure is good the refinement suffered from the low intensity of the data set, a result of the thinness of the crystals. Complete details on the crystal structure investigations, including atomic coordinates, thermal parameters and complete bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK). Copies can be obtained on request by quoting the publication citation and the deposition number CCDC 116431.

Crystal data:

C73H56N4Co•CH3OH•CH2Cl2, crystal size 0.4 × 0.15 × 0.05 mm, FW = 1181.11, triclinic, space group P1, a = 9.5157(5) Å, 17.3614(9) Å, c = 17.6891(9) Å, α = 88.445(1)°, β = 83.292(1)°, γ = 82.472(1)°, V = 2877.1(3) Å3, Z = 2, dcalc = 1.362 Mg.m-3, μ = 0.446 mm-1, Tmin = 0.84, Tmax = 0.98, θmax = 28.31°, 17447 reflection collected, 12112 independent reflections (Rint = 0.07), 5904 reflections with I > 2σ(I), 761 parameter, Δ/Δmax = 0.846 e Å-3, R1 [I > 2σ(I)] = 0.1107, R1 (all data) = 0.215, wR2 (all data) = 0.2666, S = 1.016.

Acknowledgements

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