# Crystal structure of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin–water–methanol (1/2/2), $C_{48}H_{38}N_4O_4 \cdot 2CH_3OH \cdot 2H_2O$

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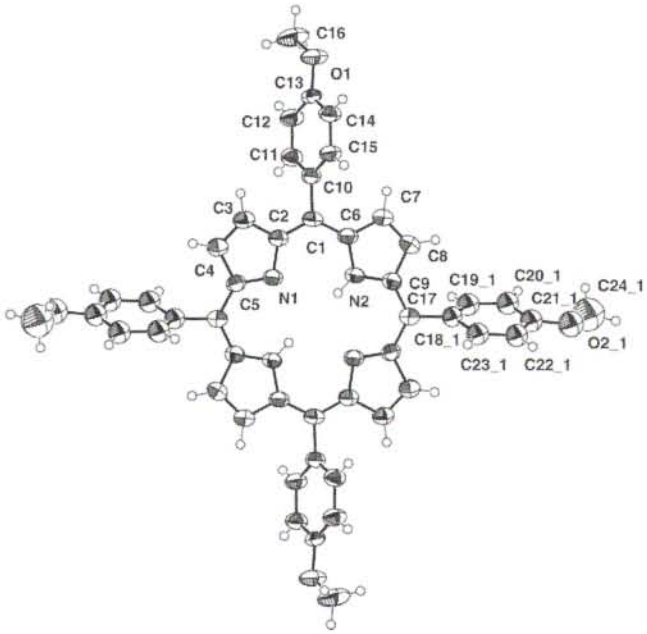


## Abstract

$C_{50}H_{50}N_4O_8$, monoclinic, $P12_1/c1$ (No. 14), $a$ = 14.272(3) Å, $b$ = 9.842(2) Å, $c$ = 15.722(3) Å, β = 100.60(5)°, $V$ = 2170.7 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.064, $R_w(F^2)$ = 0.170, $T$ = 293 K.

## Source of material

5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin was synthesized by a modified Rothemund method [1]. Small crystals were grown by slow evaporation from a water/methanol solution. Characterization after purification, before crystallization: Anal./Calc. for $C_{48}H_{38}N_4O_4$: C 78.5; H 5.2; N 7.6, found: C 78.4; H 5.4; N 7.3.

## Discussion

The structure was solved by direct methods. One of the two symmetry independent methoxyphenyl groups is disordered over two positions corresponding to a rotation of 168(3)° of the methoxy group. The disordered methoxyphenyl group was refined as two fragments with site occupations $x$ (C18_1,..., C24_1) and 1–$x$ (C18_2,...C24-2), $x$ = 0.480(15). The fragments were restrained to have similar geometry using the SAME instruction of SHEXL-97, and a DELU restraint on the displacement parameters was used in order to reduce the large correlations between the position and displacement parameters. The hydrogen atoms of the porphyrin molecule were placed at calculated positions and refined as riding using the SHELXL-97 defaults: N–H = 0.86 Å, $C_{sp2}$–H = 0.93 A, $C_{sp3}$–H = 0.96 Å. It was not possible to locate the hydrogen atoms of the highly disordered water and methanol molecules. 5,10,15,20-Tetrakisarylporphyrin showed interesting properties as biomimetic catalists of cytochrome P-450 [2], as photosensitizers in cancer phototerapy [3] and in molecular electronics [4]. Recently, we made significant improvements on the synthesis of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin [1], and it proved to be a good sensitiser to generate singlet oxygen by photoacustic calorimetry. The porphyrin is located at an inversion center. Bond lenghts and angles are unexceptional. The solvent molecules are located in voids left in the crystal packing of the macrocycles and show large displacement parameters typical of disorder.

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**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | violet plate, size 0.06 x 0.54 x 0.59 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| μ: | 0.87 cm$^{-1}$ |
| Diffractometer, scan mode: | Enraf-Nonius CAD4, profile data from ω/2θ scans |
| $2\theta_{max}$: | 44.88° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 8349, 2799 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 1540 |
| $N(param)_{refined}$: | 357 |
| Programs: | CAD4 software [5], SDP-plus [6], SHELXL-97 [7], ORTEP [8] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | Occ. | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(2) | 4e | | 0.9315 | –0.0311 | 0.5331 | 0.057 |
| H(8) | 4e | | 0.6711 | –0.1253 | 0.5632 | 0.092 |
| H(7) | 4e | | 0.7622 | –0.0620 | 0.7043 | 0.089 |
| H(3) | 4e | | 1.1209 | 0.0768 | 0.8240 | 0.075 |
| H(4) | 4e | | 1.2635 | 0.1141 | 0.7601 | 0.082 |
| H(11) | 4e | | 0.9432 | 0.2349 | 0.8013 | 0.065 |
| H(12) | 4e | | 0.8996 | 0.2662 | 0.9342 | 0.086 |
| H(14) | 4e | | 0.8728 | –0.1342 | 0.9575 | 0.082 |
| H(15) | 4e | | 0.9106 | –0.1656 | 0.8221 | 0.078 |
| H(16A) | 4e | | 0.8359 | 0.1988 | 1.1317 | 0.133 |
| H(16B) | 4e | | 0.8086 | 0.2645 | 1.0397 | 0.133 |
| H(16C) | 4e | | 0.9161 | 0.2458 | 1.0822 | 0.133 |
| H(191) | 4e | 0.48(2) | 1.4045 | –0.0104 | 0.5995 | 0.079 |
| H(201) | 4e | 0.48 | 1.5559 | 0.0838 | 0.6379 | 0.078 |

**Table 2.** Continued.

| Atom | Site | Occ. | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(221) | 4e | 0.48 | 1.4408 | 0.4217 | 0.7093 | 0.080 |
| H(231) | 4e | 0.48 | 1.2912 | 0.3411 | 0.6523 | 0.073 |
| H(24A) | 4e | 0.48 | 1.7384 | 0.2849 | 0.7648 | 0.207 |
| H(24B) | 4e | 0.48 | 1.7006 | 0.2066 | 0.6784 | 0.207 |
| H(24C) | 4e | 0.48 | 1.6761 | 0.1539 | 0.7659 | 0.207 |
| H(192) | 4e | 0.52 | 1.3857 | –0.0443 | 0.5603 | 0.080 |

**Table 2.** Continued.

| Atom | Site | Occ. | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|---|
| H(202) | 4e | 0.52 | 1.5444 | –0.0112 | 0.6210 | 0.103 |
| H(222) | 4e | 0.52 | 1.4813 | 0.3491 | 0.7092 | 0.085 |
| H(232) | 4e | 0.52 | 1.3218 | 0.3097 | 0.6558 | 0.079 |
| H(24D) | 4e | 0.52 | 1.7132 | 0.2672 | 0.7847 | 0.187 |
| H(24E) | 4e | 0.52 | 1.6115 | 0.3332 | 0.7715 | 0.187 |
| H(24F) | 4e | 0.52 | 1.6774 | 0.3583 | 0.7034 | 0.187 |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | Occ. | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(1) | 4e | | 0.9531(3) | 0.0136(4) | 0.7071(2) | 0.058(3) | 0.046(2) | 0.034(2) | 0.002(2) | 0.017(2) | 0.003(2) |
| N(1) | 4e | | 1.0764(2) | 0.0507(3) | 0.6178(2) | 0.052(2) | 0.045(2) | 0.038(2) | –0.003(2) | 0.016(2) | –0.002(2) |
| C(2) | 4e | | 1.0455(3) | 0.0461(4) | 0.6962(2) | 0.055(3) | 0.040(2) | 0.036(2) | 0.000(2) | 0.014(2) | 0.001(2) |
| N(2) | 4e | | 0.8819(2) | –0.0443(3) | 0.5560(2) | 0.055(2) | 0.054(2) | 0.037(2) | –0.009(2) | 0.020(2) | –0.005(2) |
| C(6) | 4e | | 0.8786(3) | –0.0295(4) | 0.6426(2) | 0.056(3) | 0.048(3) | 0.038(2) | –0.002(2) | 0.018(2) | –0.002(2) |
| C(8) | 4e | | 0.7344(3) | –0.0973(5) | 0.5745(3) | 0.053(3) | 0.082(3) | 0.053(3) | –0.009(3) | 0.022(2) | –0.006(2) |
| C(7) | 4e | | 0.7850(3) | –0.0632(5) | 0.6526(3) | 0.061(3) | 0.079(3) | 0.041(2) | –0.009(3) | 0.020(2) | –0.006(2) |
| C(3) | 4e | | 1.1238(3) | 0.0738(4) | 0.7654(3) | 0.063(3) | 0.052(3) | 0.037(2) | 0.001(2) | 0.011(2) | 0.004(2) |
| C(9) | 4e | | 0.7948(3) | –0.0830(4) | 0.5122(3) | 0.051(3) | 0.051(3) | 0.044(2) | –0.004(2) | 0.016(2) | –0.004(2) |
| C(17) | 4e | | 1.2323(3) | 0.1008(4) | 0.5778(2) | 0.054(3) | 0.055(3) | 0.039(2) | –0.001(2) | 0.014(2) | –0.001(2) |
| C(5) | 4e | | 1.1715(3) | 0.0814(4) | 0.6377(2) | 0.051(3) | 0.047(3) | 0.036(2) | –0.001(2) | 0.009(2) | –0.002(2) |
| C(4) | 4e | | 1.2023(3) | 0.0949(5) | 0.7306(3) | 0.060(3) | 0.063(3) | 0.040(2) | –0.003(2) | 0.010(2) | 0.005(2) |
| C(10) | 4e | | 0.9311(3) | 0.0315(4) | 0.7967(2) | 0.056(3) | 0.044(3) | 0.036(2) | –0.004(2) | 0.016(2) | –0.001(2) |
| C(11) | 4e | | 0.9278(3) | 0.1598(4) | 0.8319(3) | 0.073(3) | 0.046(3) | 0.047(3) | –0.007(2) | 0.021(2) | 0.002(2) |
| C(12) | 4e | | 0.9021(3) | 0.1790(4) | 0.9119(3) | 0.088(3) | 0.043(3) | 0.046(3) | –0.003(2) | 0.025(2) | –0.005(2) |
| C(13) | 4e | | 0.8803(3) | 0.0689(4) | 0.9577(2) | 0.063(3) | 0.056(3) | 0.030(2) | –0.009(2) | 0.015(2) | –0.007(2) |
| C(14) | 4e | | 0.8854(3) | –0.0594(5) | 0.9253(3) | 0.077(3) | 0.052(3) | 0.040(2) | –0.008(2) | 0.023(2) | 0.001(2) |
| C(15) | 4e | | 0.9093(3) | –0.0783(4) | 0.8444(2) | 0.078(3) | 0.043(3) | 0.039(2) | –0.006(2) | 0.022(2) | –0.005(2) |
| O(1) | 4e | | 0.8533(2) | 0.0752(3) | 1.0371(2) | 0.111(3) | 0.064(2) | 0.041(2) | –0.002(2) | 0.035(2) | –0.005(2) |
| C(16) | 4e | | 0.8535(5) | 0.2070(6) | 1.0759(3) | 0.146(5) | 0.076(4) | 0.051(3) | 0.010(4) | 0.036(3) | –0.017(3) |
| C(181) | 4e | 0.48(2) | 1.330(1) | 0.160(3) | 0.611(3) | 0.067(8) | 0.05(1) | 0.05(1) | –0.005(7) | 0.03(1) | –0.00(1) |
| C(191) | 4e | 0.48 | 1.411(1) | 0.080(2) | 0.616(2) | 0.073(9) | 0.07(1) | 0.05(1) | 0.003(6) | 0.004(6) | –0.018(8) |
| C(201) | 4e | 0.48 | 1.502(1) | 0.133(2) | 0.644(1) | 0.061(7) | 0.08(1) | 0.05(1) | 0.010(7) | 0.010(8) | –0.016(9) |
| C(211) | 4e | 0.48 | 1.5112(9) | 0.260(2) | 0.682(1) | 0.048(7) | 0.08(1) | 0.062(8) | –0.003(7) | 0.023(8) | –0.010(8) |
| C(221) | 4e | 0.48 | 1.4340(9) | 0.336(2) | 0.684(1) | 0.052(6) | 0.08(1) | 0.068(7) | 0.000(6) | 0.019(6) | –0.024(8) |
| C(231) | 4e | 0.48 | 1.344(1) | 0.287(2) | 0.650(3) | 0.054(7) | 0.07(1) | 0.059(8) | –0.009(7) | 0.018(9) | –0.02(1) |
| O(21) | 4e | 0.48 | 1.5998(8) | 0.317(1) | 0.7193(6) | 0.051(6) | 0.096(8) | 0.108(7) | –0.004(5) | 0.011(5) | –0.020(5) |
| C(241) | 4e | 0.48 | 1.686(2) | 0.233(3) | 0.733(2) | 0.06(1) | 0.21(3) | 0.14(2) | 0.05(1) | 0.01(1) | 0.04(2) |
| C(182) | 4e | 0.52 | 1.334(1) | 0.122(2) | 0.610(3) | 0.041(7) | 0.06(1) | 0.039(9) | 0.012(5) | –0.003(6) | 0.009(9) |
| C(192) | 4e | 0.52 | 1.4036(8) | 0.032(2) | 0.594(2) | 0.048(6) | 0.09(1) | 0.07(1) | 0.008(6) | 0.017(6) | –0.023(7) |
| C(202) | 4e | 0.52 | 1.4991(8) | 0.054(2) | 0.628(1) | 0.049(6) | 0.08(1) | 0.13(1) | 0.017(6) | 0.018(6) | –0.019(9) |
| C(212) | 4e | 0.52 | 1.5266(9) | 0.172(2) | 0.673(1) | 0.042(5) | 0.12(1) | 0.05(1) | 0.004(6) | –0.001(6) | –0.016(9) |
| C(222) | 4e | 0.52 | 1.462(1) | 0.267(2) | 0.682(1) | 0.052(7) | 0.09(1) | 0.079(8) | –0.009(7) | 0.028(9) | –0.026(9) |
| C(232) | 4e | 0.52 | 1.366(1) | 0.243(2) | 0.650(2) | 0.050(6) | 0.08(1) | 0.07(1) | 0.002(7) | 0.020(8) | –0.01(1) |
| O(22) | 4e | 0.52 | 1.6222(7) | 0.185(1) | 0.6990(7) | 0.042(5) | 0.17(1) | 0.137(8) | 0.002(5) | –0.008(5) | –0.033(7) |
| C(242) | 4e | 0.52 | 1.659(1) | 0.293(3) | 0.743(2) | 0.024(9) | 0.17(2) | 0.17(2) | –0.03(1) | –0.01(1) | –0.01(2) |
| O(3) | 4e | | 0.438(2) | –0.167(2) | 1.064(1) | 0.60(3) | 0.31(2) | 0.26(2) | –0.18(2) | 0.22(2) | –0.07(1) |
| O(4) | 4e | | 0.4287(8) | 0.011(1) | 0.9792(7) | 0.45(2) | 0.27(1) | 0.19(1) | 0.01(2) | 0.08(1) | –0.130(9) |
| C(25) | 4e | | 0.543(2) | –0.161(2) | 1.0967(9) | 0.35(2) | 0.28(2) | 0.13(1) | 0.07(2) | 0.07(1) | –0.06(1) |

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