X-ray Structures of a Phenanthroline-Strapped Porphyrin and Its Dihydrated Zinc(II) Complex: Convergent Distal Hydrogen Bonds and "CH···O" Interactions

Philippe Ochsenbein,[a] Michel Bonin,[b] Kurt Schenk,[b] Jérôme Froidevaux,[c] Jennifer Wytko,[c] Ernest Graf,[d] and Jean Weiss*[c]

Dedicated to the memory of Dr. Michael Momenteau

Keywords: Hydrogen bonds / Inclusion compounds / Solid-state structures / Porphyrinoids / Zinc

The X-ray structure of a phenanthroline-(phen-)strapped 1,10-diphenylporphyrin **1** has been resolved. From the structure obtained, it is apparent that in spite of the rigidity of the strap the porphyrin ring is only slightly distorted, and that the substituents on the phen moiety define what would seem to be a hydrophobic pocket. Metallation of the free base **1** with zinc(II) acetate yields a metallic complex (**1**)Zn with a free axial coordination site. Crystallization of the zinc complex in the presence of a hindered base (*N*-methylimidazole, denoted *N*-MeIm) in organic solvents affords single crystals of a porphyrinatozinc(II) species, in which two water molecules are surprisingly present in the encumbered (distal) pocket of the phen site. One water molecule is axially bound to the zinc(II) ion, while the other is doubly hydrogen-bonded, as an H-bond donor to the phenanthroline and as an H-bond acceptor to the axial water ligand.

Introduction

Metalloporphyrins capable of forming hydrogen bonds (H bonds) have been extensively studied due to their involvement in photosynthetic processes of higher plants, either as main pigments such as chlorophyll a, or as accessory pigments such as chlorophyll b. Zinc and magnesium porphyrins and chlorin derivatives constitute the majority of models studied to date. H-bond formation can occur either at the periphery of the tetraaza ligand or along the axis defined by the metal $4p_z$ and $4d_{z^2}$ orbitals, but in either case is associated with selective assembling processes. These assembling processes include substrate recognition[1] and axial ligand selection (e.g. CO/O_2),[2] dimer formation,[3] and anchoring to proteins and membranes.[4][5] Water molecules may play a crucial role in bridging H-bond donors and H-bond acceptors, leading to superstructures;[6] thus, H bonding may originate from a water molecule coordinated axially to a metalloporphyrin.

An example of a self-assembling process of a porphyrin derivative mediated by an axially bound water molecule, leading to a dimeric porphyrin−quinone assembly, has recently been described by Fajer.[7] This type of interaction has been envisaged for decades,[8] and analysis of several metalloporphyrin structures, including those of mono-[9] and dihydrated[10] chlorophyll, has suggested that hydrogen bonding plays an important role in the anchoring of pigments on proteins. A confirmation of the role of water in the three-dimensional structure of a peridin-chlorophyll light-harvesting complex was reported by Hofmann and Welte.[11] In this case, a histidine imidazole ring of the pigment, which is stacked with ring II of the chlorophyll, is H-bonded through a water molecule coordinated at the central Mg. Coordination of water to the central metal in pigments may also be involved in the modification and control of the redox properties of charged radical intermediate species.[12] Thus, H bonding contributes in various ways to a better control of electron transfer in natural systems,[13] and in this regard it is important that well-defined hydrated structures of metalloporphyrins are obtained. In this paper, we present the structure of a dihydrated zinc porphyrin complex, together with that of the corresponding free base.[14]

In a search for controlled architectures combining porphyrins and either metal- or H-binding sites, we have described the synthesis of a phenanthroline-(phen-)strapped porphyrin **1**.[14] The formation of copper and silver mixed-valence complexes with this heteroditopic ligand has illustrated its coordination capabilities.[15] In the course of the synthesis of a heterodinuclear zinc-copper complex of ligand **1**, we found that it was possible to crystallize the free base and the dihydrated zinc(II) complex. The X-ray structures[16] of both are described and compared herein. Moreover, the H-bond network of the two water molecules found

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[a] Synthélabo Recherche,
10, rue des Carrières, F-92500 Rueil-Malmaison, France
[b] Département Sciences Physiques, Université de Lausanne,
CH-1015 Lausanne-Dorigny, Switzerland
[c] Laboratoire d'Electrochimie, UMR 7512 au CNRS, Université Louis Pasteur,
4, rue Blaise Pascal, F-67070 Strasbourg, France
Fax: (internat.) + 33-3/88611553
E-mail: jweiss@chimie.u-strasbg.fr
[d] Laboratoire de Chimie de Coordination Organique, UMR 7513 au CNRS, Université Louis Pasteur,
4, rue Blaise Pascal, F-67070 Strasbourg, France

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in the hydrophobic environment of the phenanthroline pocket in the case of the Zn^{II} porphyrin is discussed.

Results and Discussion

Crystals of the free base **1** were obtained by slow diffusion of hexane and traces of methanol into a concentrated (10^{-2} M) solution of the porphyrin in dichloromethane. The structure depicted in Figure 1 clearly shows that the tetrapyrrolic macrocycle is only slightly distorted.

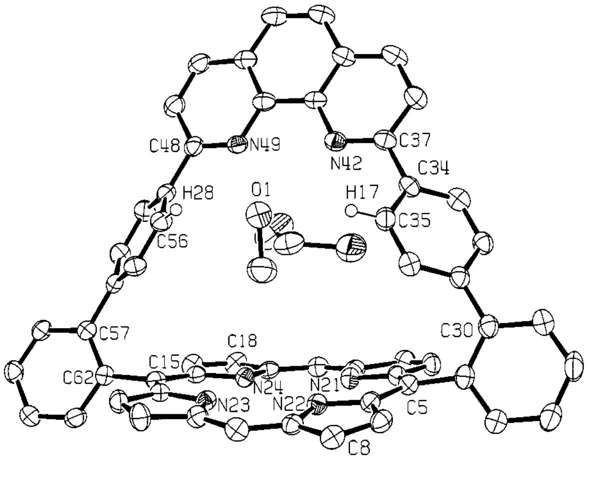

Figure 1. Crystallographic view of **1**; hydrogen atoms are omitted for the sake of clarity and only atoms discussed in the text are labelled; selected bond lengths and angles are discussed in the text

There had previously been some doubt as to the degree of planarity of the porphyrin ring, as the rate of metallation of **1** is three orders of magnitude faster than that of regular tetraphenylporphyrin (TPP).[15] The deviation from planarity shows that the conformation adopted by the (24-atom) core is saddled with respect to the orientation of the pyrrole rings and ruffled when considering the *meso* positions [maximum deviation from planarity of 0.24 Å for the *meso*-(C5) and β-carbon atoms (C8)]. The phenyl spacers between the porphyrin and phenanthroline units are tilted away from the phen plane (by 41° and 49°), which is in agreement with previously reported 2,9-diphenylphenanthroline structures.[17] The frozen orientation of the phenyl spacers is observed only in the solid state; ^{1}H-NMR data are consistent with their free rotation in solution. A tilt of the strap towards one side of the porphyrin is also seen in the crystal, while solution ^{1}H-NMR data are consistent with a mirror plane containing the phen subunit (apparent C_{2v} symmetry).[14] The cleft, or cavity, defined by the two phenyl spacers should be referred to as the distal pocket, in accordance with standard mono-*ansa*-porphyrin nomenclature. The width of this pocket is ca. 11.0 Å (C30−C57) above the porphyrin plane (between the two *meso*-phenyl groups), and ca. 6.7 Å (C37−C48) near the phenanthroline unit (between the two phenyl spacers in the 2- and 9-positions of the phen). A methanol guest molecule resides in the pocket, held in position by a set of four weak interactions. There are two hydrogen bonds to the phenanthroline nitrogen atoms, with distances of 3.19(2) Å between O1 (methanol) and N42 and 3.21(2) Å between O1 and N49. In addition, two strong "CH···O" interactions[23] are present between O1 and C35−H17 and C56−H28 with H···O distances (CHO angles) of 2.41(2) Å (147.7°) and 2.45(2) Å (139.4°), respectively. As depicted in the unit-cell view (Figure 2), intermolecular π interactions may be responsible for the bending of the phen strap. This distortion of the free base cannot be guest-induced, as might be the case for the corresponding zinc(II)-imidazole complex and for the dihydrated porphyrinatozinc(II) complex (vide infra).

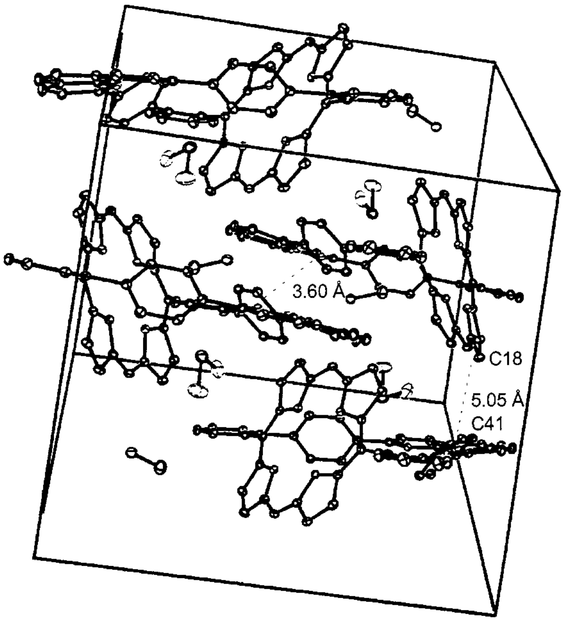

Figure 2. Packing of **1** in the unit cell; additional methanol molecules occupy free spaces defined by the head-to-tail arrangement of **1**

A π-stacking interaction at van der Waals distances is present between two phenyl spacers of neighboring molecules, with maximum and minimum interplanar distances of 3.611(4) and 3.590(4) Å for C34 and C35, respectively, from the mean plane of the neighboring phenyl spacer. As depicted in Figure 2, these two particular aromatic rings are parallel in the solid state, with a dihedral angle of 0.00(9)° and a centroid−centroid distance of 3.807(5) Å. Edge-on (or T-shaped) σ−π interactions[19] between the *meso* and β positions of one porphyrin unit and the phen nucleus of another are also observed with, for example, a minimum distance of 5.03(5) Å between C18 and C41 (see Figure 2). The structure of the free base would appear to be well-suited for the formation of mixed-valence homobinuclear complexes, as reported previously.[15] Moreover, due to the allowed bending of the phen strap, the inclusion of substrates within the cleft, already observed for monometallic species,[18] should also be possible in a bimetallic complex.

Metallation of the free base with zinc acetate in refluxing DMF afforded [(**1**)Zn(H_2O)$_2$] in 80% yield after purification by chromatography on alumina (CH_2Cl_2 + traces of pyridine).[19] Crystals of [(**1**)Zn(H_2O)$_2$] were obtained by diffusion of hexane into a dilute solution of (**1**)Zn in dichloromethane containing one equivalent of *N*-methylimidazole

(*N*-MeIm). Initially, *N*-MeIm was added to complete the coordination sphere of zinc(II) on the expected proximal side of the porphyrinatozinc(II) species, but subsequent binding studies revealed a low affinity of *N*-MeIm for the zinc complex.[18] Instead, the coordination sphere of the pentacoordinated zinc(II) cation is completed by an oxygen atom of a water molecule, as depicted in Figure 3.

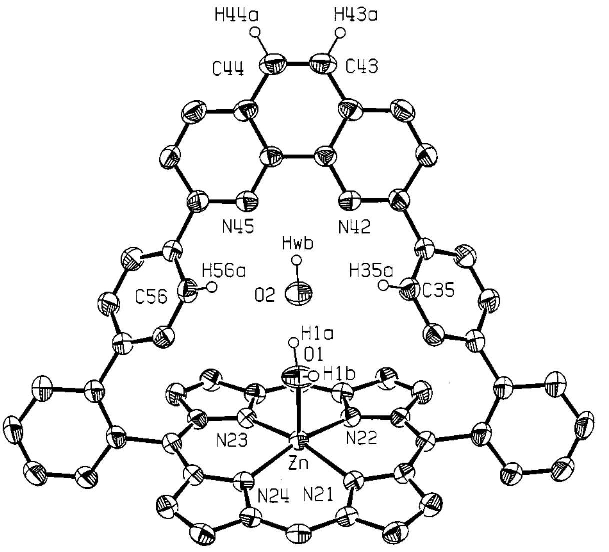

Figure 3. Front view and selected atom numbering for [(**1**)Zn(H_2O)$_2$]; only the hydrogen atoms involved in the H-bond network found by Fourier difference techniques are represented; selected bond lengths and angles are discussed in the text

The conformation of the porphyrin (24-atom) core is changed from ruffled in the solid state to domed, as would be expected for the coordination of large metal cations. This variation of conformation of the (24-atom) core does not affect the phenanthroline strap, the distance between the two *meso*-carbon atoms remaining unchanged. This confirms that no conformational restraints are imposed by the rigid phen strap. The unexpected presence of two water molecules within the distal pocket merits special comment.

The slightly domed porphyrin ring bears a resemblance to reported conformations of pentacoordinated zinc porphyrin complexes with oxygen donors occupying the fifth coordination site.[2,7,9a,9b,12,22] The coordination sphere around the zinc(II) atom is a slightly distorted tetragonal pyramid. The Zn−O1 bond [2.09(2) Å] is perpendicular to the (24-atom) core in that the N−Zn−O1 angles for N21 to N24 are 98.58(8), 98.52(8), 98.34(8), and 98.19(8)°, respectively. While the hydrogen atoms were added to the ligand using a routine treatment of the data, high resolution of the structure allowed us to establish the precise locations, by Fourier difference analysis (see Crystallographic Studies), of the two hydrogen atoms of the axially bound water molecule, as well as that remotely bound to the phenanthroline moiety. As depicted in Figure 3, the plane containing the axial water molecule is orthogonal to the phen plane and is oriented above the unsubstituted $C_{meso}-C_{meso}$ axis with an H1a−O1−H1b angle of 108(3)° and Zn−O1−H1a and Zn−O1−H1b angles of 126(2)° and 123(2)°, respectively. The O1−H1b bond length of 0.92(2) Å is slightly shorter than the O1−H1a distance [0.97(2) Å] due to the hydrogen bonding of H1a with O2. The detailed drawing of the H-bond network given in Figure 4 shows that the 1.69(2) Å distance between H1a and O2 corresponds to a strong H bond, with an oxygen−oxygen distance of 2.621(2) Å.

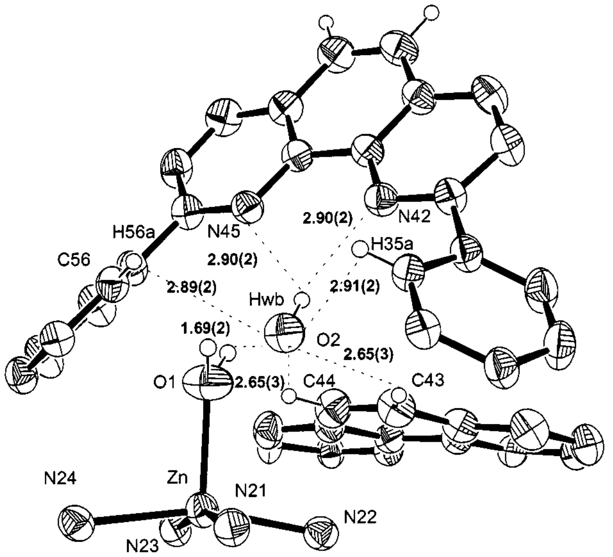

Figure 4. Crystallographic detail of the H-bond (3) and "CH···O" (4) interactions; the direct environment of the O2 water oxygen atom is represented; only the parts of the molecules involved in the binding are depicted; distances are given in Å; an additional van der Waals contact is observed between C44 and C43 and the porphyrin plane (C10) with equal distances of 3.40(2) Å

The angle of 114(2)° between H1a and the uncoordinated O2−Hwb bond, coupled with the precise location of Hwb at 2.27(3) and 2.21(3) Å from the phen nitrogen atoms N42 and N45, respectively, would seem to indicate that there is a direct interaction between H1a and the uncoordinated oxygen lone pairs, and that the second hydrogen atom of the uncoordinated water molecule is disordered in the crystal. This water molecule is fixed in the crystal by means of four "CH···O" interactions.[23] Two bonds of this type are found between the uncoordinated oxygen atom and the two top-central carbon atoms (C44 and C43) of the neighboring adjacent phenanthroline backbone, with identical H···O distances of 2.65(3) Å. The other two "CH···O" interactions are found between the aromatic *ortho* protons of the phenyl spacer and the uncoordinated oxygen atom, with shorter H···O distances of 2.89(2) and 2.91(2) Å. The three hydrogen bonds and four "CH···O" interactions are depicted in detail in Figure 4.

The packing of the metalloporphyrin in the crystal, as depicted in Figure 5, shows that additional π interactions are also present, mainly between the phenanthroline nuclei and open faces of the porphyrin rings. Each porphyrin unit resides on the phen strap of the molecule below, thereby forming Z-shaped stacks (a herringbone arrangement) of porphyrin units. The stacks are mutually interpenetrated by a partial overlap of the back of the phen moiety with the unsubstituted edge of the porphyrin ring in the next stack, which allows the formation of the inter-stack "CH···O" interactions described above. As indicated in Figure 5, distances corresponding to strong aromatic-ring-stacking interactions, as well as edge-on interactions are observed within and between the zig-zag columns of the porphyrin units.

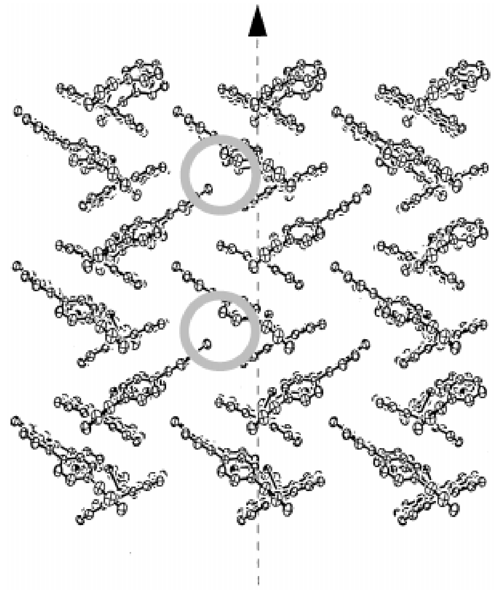

Figure 5. Packing of [(**1**)Zn(H_2O)$_2$]; the crystal consists of parallel arrangements of layers made up of zig-zag stacks (along the --- axis) of [(**1**)Zn(H_2O)$_2$] connected by "CH···O" interactions (identified by grey circles for the left stack); CH_2Cl_2 molecules are omitted for the sake of clarity

The presence of these additional intermolecular interactions certainly contributes in making the observed "CH···O" interactions quite strong (C···O distance: ca. 3.29 Å; CHO angle: ca. 124°) compared to the range of strengths previously reported in the literature.[24] Indeed, the particular nature of the C44−C43 bond in the phenanthroline defines the H44 and H43 atoms involved in the "CH···O" bond as vinylic protons rather than aromatic protons, which usually exhibit "C···O" distances in the range 3.55 to 3.65 Å,[25] with CHO angles commonly in the range 140−180°.[26]

A possible explanation for the high affinity for water shown by the hindered side of the porphyrin ligand is that the coordination of water does not induce any major conformational changes in the ligand. Indeed, the tilt of the *meso*-phenyl substituents on the porphyrin ring in the free base is very similar to that observed in the dihydrated zinc(II) complex. The measured dihedral angles between the *meso*-phenyl groups and the porphyrin plane are 67.86(6)° and 72.07(8)° in the zinc(II) complex and 66.83(10)° and 71.14(11)° in the free base. Furthermore, the dihedral angle between the phen subunit and the porphyrin core remains unchanged during the metallation/hydration process (ca. 61°). Thus, the energetic requirements for accommodating the two water molecules are minimized. Moreover, the lipophilic nature of the solvent (CH_2Cl_2) in which the crystals were grown might have been more conducive to *O* coordination of water at the zinc center than to *N* coordination of the imidazole.

Conclusion

The structure of a mono-*ansa*-porphyrin bearing a phenanthroline strap maintained at a fixed distance by means of two phenyl spacers has been resolved, as has that of the corresponding zinc(II) complex. The structure of the free base shows a relatively large cavity within the strap, with a distance of approximately 6 Å between the two coordination sites. The structure of the zinc complex obtained in the presence of *N*-MeIm does not show binding of an axial nitrogen ligand, but two water molecules are found to be present in the phenanthroline pocket. One water molecule is axially bound to the zinc atom, while the second completes the hydrogen-bond "network" to the phenanthroline nitrogen atoms. Experiments to determine the affinity of **1** for water in solution and the exchange rate of water are currently in progress, as are investigations in which the zinc ion is replaced by a magnesium ion to allow comparison of the photophysical properties of metalloporphyrin cores in the presence and absence of coordinated water.

Experimental Section

General: All solvents and reagents used were of commercial analytical grade. − Ligand **1** was prepared according to ref.[14] − ^{1}H-NMR spectra were recorded with a Bruker WP 300 MHz instrument; data were processed using WINNMR software available from Bruker, with residual non-deuteriated solvent as chemical-shift reference (CH_2Cl_2 at δ = 5.29). − UV/Vis spectra were recorded with a Hewlett-Packard HP8452A diode-array spectrophotometer (2 nm resolution).

[1(Zn)]: To a solution of the free base **1** (50 mg, $6.5 \cdot 10^{-5}$ mol) in 20 mL of DMF was added Zn(OAc)$_2$ (100 mg, $45.5 \cdot 10^{-5}$ mol) and the solution was refluxed under argon until the Soret band at 412 nm had disappeared from the UV/Vis spectra of withdrawn aliquots (ca. 4 h). The resulting mixture was then poured into water (200 mL). The pink-red precipitate was collected by filtration, washed with water, and dried by azeotropic distillation with toluene and ethanol, to afford the pure zinc(II) complex as a red solid (47 mg, $5.5 \cdot 10^{-5}$ mol, 85%); m.p. > 250 °C. − ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 10.15 (s, 2 H), 9.28 (d, *J* = 4.4 Hz, 4 H), 9.01 (d, *J* = 4.4 Hz, 2 H), 8.75 (d, *J* = 7.4 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 2 H), 7.89 (m, 6 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.48 (s, 2 H), 6.62 (d, *J* = 8.3 Hz, 4 H), 6.51 (d, *J* = 8.3 Hz, 4 H). − [**1**(Zn)] + CH_2Cl_2 + 3/2 H_2O: $C_{57}H_{37}Cl_2N_6O_{1.5}Zn$ (968.2): calcd. C 70.86, H 3.86, N 8.70; found C 71.06, H 4.02, N 8.72. − UV/Vis (CH_2Cl_2): λ_{max} [nm] (ε [$M^{-1} \cdot cm^{-1}$]): 284 (28000), 308 (29000), 418 (259000), 546 (11000), 578 (2000). − Positive-ion FAB MS; *m/z*: calcd. for $[M]^+ = [C_{56}H_{32}N_6Zn]^+$ 852; found 853.

X-ray Crystallographic Study:[16] Crystals of **1** were obtained by vapor diffusion of hexane into a CH_2Cl_2/MeOH (95:5) solution of the porphyrin. Crystal data for $C_{56}H_{34}N_6 \cdot CH_2Cl_2 \cdot CH_3OH$: M_r = 907.91, monoclinic, space group $P2_1/c$, a = 17.763(5), b = 16.800(4), c = 15.759(3) Å, β = 111.59(2)°, V = 4372(3) Å^3, Z = 4, $\rho_{calcd.}$ = 1.38 gcm^{-3}, μ(Cu-K_α) = 1.743 mm^{-1}. Data were collected with a Philips PW 1100/16 diffractometer using Cu-K_α

graphite-monochromated radiation ($\lambda = 1.5418$ Å) at −100°C. A dark-red crystal of dimensions $0.40 \times 0.40 \times 0.40$ mm was used and a total of 5517 reflections were collected, $3° < \theta < 53°$ (max θ limited by cooling device). 4178 reflections with $I > 3\sigma(I)$ were used for the structure determination and refinement. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. Empirical absorption corrections, transmission factors: 0.64, 1.00. For all computations, the Nonius OpenMoleN package[20] was used. Final results: $R_f = 0.052$, $wR\ (F) = 0.080$, GooF on F: 1.537, maximum residual electronic density: 0.58 eÅ^{-3}. Crystals of [(**1**)Zn(H_2O)$_2$] were obtained by slow diffusion of hexane into a dichloromethane solution of (**1**)Zn containing one equivalent of *N*-methylimidazole. − Crystal structure of [(**1**)Zn(H_2O)$_2$]: $C_{57}H_{35}Cl_2N_6O_2Zn$, $M_r = 972.18$, red rectangular plates, monoclinic, space group *Ia*, $a = 12.355(3)$, $b = 12.658(3)$, $c = 28.639(6)$ Å, $\beta = 89.99(3)°$, $V = 4479(3)$ Å^3, $Z = 4$. Data were collected at room temperature with a STOE-IPDS diffractometer using Mo-K_α graphite-monochromated radiation ($\lambda = 0.70910$ Å). Structure solution and anisotropic refinement were performed with the SHELXTL package[21] using 6664 independent reflections of the 14456 reflections collected. Hydrogen atoms were geometrically positioned with all distances X−H being free to refine, except for those attached to oxygen atoms, which were located by Fourier difference techniques. Final results: $R_1 = 0.0342$ [$I > 2\sigma(I)$], $wR_2 = 0.0865$ (all data), GooF on F^2: 1.342, maximum residual density: 0.405 eÅ^{-3}.

Acknowledgments

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[1] T. Mizutani, T. Kurahashi, T. Murakami, N. Matsumi, H. Ogoshi, *J. Am. Chem. Soc.* **1997**, *119*, 8991−9001.

[2] K. M. Barkigia, D. Melamed, R. M. Sweet, K. M. Smith, J. Fajer, *Spectrochim. Acta, Part A* **1997**, *53*, 463−469.

[3] [3a] M. F. Perutz, *Ann. Rev. Biochem.* **1979**, *48*, 327−386 and references cited therein. − [3b] M. Momenteau, C. A. Reed, *Chem. Rev.* **1994**, *94*, 659.

[4] O. El-Kabbani, C.-W. Chang, D. Tiede, J. Norris, M. Schiffer, *Biochemistry* **1991**, *30*, 5361−5369.

[5] [5a] E. J. Bylina, C. Kirmaier, L. McDowell, D. Holten, D. C. Youvan, *Nature* **1988**, *336*, 182−184 and references cited therein. − [5b] W. Kühlbrandt, D. N. Wang, *Nature* **1991**, *350*, 130−134.

[6] L. R. McGilliwray, J. L. Atwood, *Nature* **1997**, *389*, 469−472.

[7] J. Fajer, K. M. Barkigia, D. Melamed, R. M. Sweet, H. Kurrek, J. von Gersdorff, M. Plato, H.-C. Rohland, G. Elger, K. Möbius, *J. Phys. Chem.* **1996**, *100*, 14236−14239.

[8] M. S. Fischer, D. H. Templeton, A. Zalkin, M. Calvin, *J. Am. Chem. Soc.* **1972**, *94*, 3613−3619. Very valuable information on H bonding and magnesium(II) or zinc(II) in porphyrins has been compiled by: K. M. Barkigia, J. Fajer in *The Photosynthetic Reaction Center* (Eds.: J. Deisenhoffer, J. R. Norris), Academic Press, San Diego, CA, **1993**, vol. II, pp. 513−539.

[9] [9a] B. Cheng, R. Scheidt, *Inorg. Chim. Acta* **1995**, *237*, 5−11. − [9b] O. C. Choon, V. McKee, G. A. Rodley, *Inorg. Chim. Acta* **1986**, *123*, 11−14. − [9c] C. Kratky, H. P. Isenring, J. D. Dunitz, *Acta Crystallogr.* **1977**, *B33*, 547−549. − [9d] R. Timkovich, A. Tulinsky, *J. Am. Chem. Soc.* **1969**, *91*, 4430−4432. − [9e] M. D. Glick, G. H. Cohen, J. L. Hoard, *J. Am. Chem. Soc.* **1967**, *89*, 1996−1998.

[10] [10a] R. Serlin, H.-S. Chow, C. E. Strouse, *J. Am. Chem. Soc.* **1975**, *97*, 7237−7242. − [10b] H.-S. Chow, R. Serlin, C. E. Strouse, *J. Am. Chem. Soc.* **1975**, *97*, 7230−7237. − [10c] C. Kratky, J. D. Dunitz, *Acta Crystallogr.* **1975**, *B31*, 1586−1589.

[11] E. Hofmann, P. M. Wrench, F. P. Sharples, R. G. Hiller, W. Welte, K. Diederichs, *Science* **1996**, *272*, 1788−1791.

[12] For X-ray studies on charged radical species, see: H. Song, R. D. Orosz, C. A. Reed, W. R. Scheidt, *Inorg. Chem.* **1990**, *29*, 4274−4282; H. Song, N. P. Rath, C. A. Reed, W. R. Scheidt, *J. Am. Chem. Soc.* **1989**, *119*, 8991−9001. For ESR and ENDOR studies, see: A. Forman, M. S. Davis, E. Fujita, L. K. Hanson, K. M. Smith, J. Fajer, *Isr. J. Chem.* **1981**, *21*, 265−269. For redox structural analysis, see: K. M. Barkigia, L. Chantranupong, K. M. Smith, J. Fajer, *J. Am. Chem. Soc.* **1988**, *110*, 7566−7567. For a global analysis, see: M. W. Renner, R. J. Cheng, C. K. Chang, J. Fajer, *J. Phys. Chem.* **1990**, *94*, 8508−8511.

[13] A. Forman, M. W. Renner, E. Fujita, K. M. Barkigia, M. C. W. Evans, K. M. Smith, J. Fajer, *Isr. J. Chem.* **1989**, *29*, 57−64.

[14] For the synthesis of the ligand, see: J. A. Wytko, E. Graf, J. Weiss, *J. Org. Chem.* **1992**, *57*, 1015−1018.

[15] A. Giraudeau, J.-P. Gisselbrecht, M. Gross, J. Weiss, *J. Chem. Soc., Chem. Commun.* **1993**, 1103−1105.

[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-113533, -113534. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[17] C. Pascard, J. Guilhem, S. Chardon-Noblat, J. P. Sauvage, *New J. Chem.* **1993**, *17*, 331−335.

[18] The presence of the phen strap allows the selective binding of imidazole and 2-methylimidazole within the phen pocket with respective log K_a values of 6.1 and 7.3, while *N*-methylimidazole is bound on the open side with a log K_a value of 4.7 under the same conditions (CH_2Cl_2, 25°C). For details, see: J. Froidevaux, P. Ochsenbein, M. Bonin, K. Schenk, P. Maltese, J.-P. Gisselbrecht, J. Weiss, *J. Am. Chem. Soc.* **1997**, *119*, 12362−12363.

[19] C. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525−5534.

[20] C. K. Fair in *MoleN, An Interactive Intelligent System for Crystal Structure Analysis*, Nonius, Delft, The Netherlands, **1990**.

[21] G. M. Sheldrick, *SHELXTL-Plus*, Rel. 5.03, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, **1995**.

[22] [22a] L. D. Spaulding, P. G. Eller, J. A. Bertrand, R. H. Felton, *J. Am. Chem. Soc.* **1974**, *96*, 982−987. − [22b] M. M. Williamson, C. M. Prosser-McCartha, S. Mukudan, Jr., C. L. Hill, *Inorg. Chem.* **1988**, *27*, 1061−1068. − [22c] C. Comte, C. P. Gros, S. Koeller, R. Guilard, D. J. Nurco, K. M. Smith, *New J. Chem.* **1998**, 621−626.

[23] For a recent paper representative of the growing importance of "CH···O" interactions in molecular recognition (and *not* in crystal engineering), see: R. A. Musah, G. M. Jensen, R. J. Rosenfeld, D. E. McRee, D. B. Goodin, *J. Am. Chem. Soc.* **1997**, *119*, 9083−9084.

[24] "CH···O" interactions in the coordination of water have been extensively analyzed: T. Steiner, W. Saenger, *J. Am. Chem. Soc.* **1993**, *115*, 4545−4547.

[25] G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441−449.

[26] T. Steiner, G. R. Desiraju,*Chem. Commun.* **1998**, 891−892.

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