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Molecular structure of (5,10,15,20-tetrabutyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II)—correlation of nonplanarity with frontier orbital shifts †

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Highly substituted porphyrins exhibit significantly distorted, nonplanar conformations in the solid state. The crystallographically determined degree of nonplanarity correlates with a bathochromic shift of the absorption maxima in solution. In addition, nonplanar porphyrins with meso aryl groups show increasing in-plane rotation of the meso aryl groups, which potentially could account for the observed changes in spectroscopic and physicochemical properties of nonplanar porphyrins. A crystal structure analysis of the title compound NiTBuOEP reveals a highly nonplanar conformation with an average deviation from planarity for the 24 macrocycle atoms of 0.462 Å and displacements of the meso carbon atoms from the 4N-plane of 1.044 Å. The average Ni–N bond distance in the crystal (1.873(3) Å) is in good agreement with the Ni–N bond distance in solution (1.87 Å) that was determined by EXAFS. Compared to more planar reference compounds, NiTBuOEP exhibits significantly red-shifted absorption spectra in solution, correctly predicted by INDO/s calculations. As the shortness of the Ni–N bonds has been shown to be an excellent indicator for the degree of conformational distortion in porphyrins, this proves that the highly nonplanar conformation of sterically strained porphyrins is maintained in solution. Thus, the physical and chemical properties measured in solution do indeed reflect the stereochemistry of the single crystals. In addition, the use of only alkyl substituents in NiTBuOEP to cause nonplanarity obviously circumvents potential electronic effects due to aryl ring interactions.

Introduction

Skeletal deformations of porphyrinic chromophores and prosthetic groups are increasingly evident in crystal structures of photosynthetic antennae,[1] reaction centers[2] and heme proteins.[3,4a] A significant effort has thus focussed on trying to assess the effects of nonplanarity on optical, redox and excited state properties using sterically encumbered synthetic porphyrins.[4–6] Although the altered physical and chemical properties of the distorted molecules certainly suggest that the nonplanar conformations found in single crystals are conserved in solution, a basic question to be answered is how faithfully these distortions are maintained in solution. We address this question by taking advantage of extended X-ray absorption fine structure (EXAFS) techniques that yield metal–nitrogen distances with a reliability of ≈0.02 A (based on previous studies) and thus allow direct comparison with crystallographic results.[6] Furthermore, in the case of low spin Ni(II) porphyrins, hydroporphyrins, and porphycenes, Ni–N bond lengths have proved to be reliable reporters of the conformations of the macrocycles: short Ni–N distances are diagnostic of nonplanar macrocycles, whereas long distances are typical of planar molecules.[6]

A different question arises[7] because of the frequent use of multiple peripheral aryl substituents to induce steric crowding.[4b,5,6] In the resulting nonplanar porphyrins (*e.g.* NiTPhOEP see Chart 1), the aryl rings are no longer orthogonal to the porphyrin plane and adopt small dihedral angles to that plane, possibly resulting in better overlap with the porphyrin π system and thus conceivably causing[7] the observed optical and redox changes attributed to conformational effects.[4b,5,6] To address this question we present here solution EXAFS and crystallographic results for the peripherally crowded, nonplanar (5,10,15,20-tetrabutyl-2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (NiTBuOEP see Chart 1).[8]

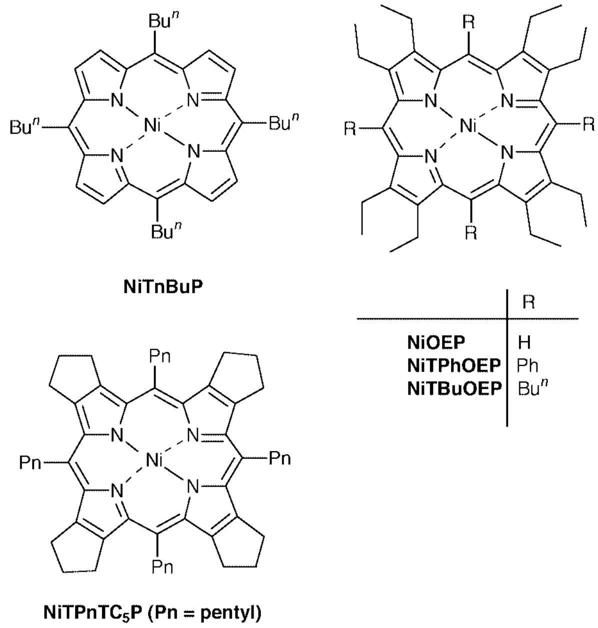

Chart 1

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† Electronic supplementary information (ESI) available: experimental details, EXAFS fitting results, X-ray absorption and EXAFS spectra. See http://www.rsc.org/suppdata/dt/a9/a905927j/

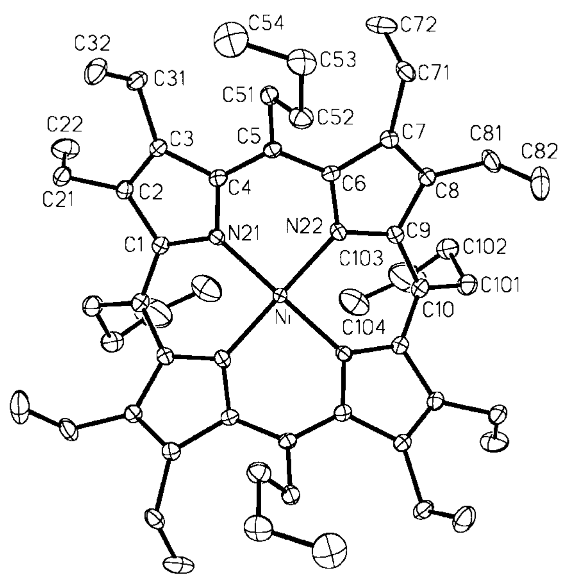

Fig. 1 Thermal ellipsoid plot (50% occupancy) of the molecular structure of NiTBuOEP in the crystal. Hydrogen atoms and disordered positions have been omitted for clarity.

The two techniques yield similar Ni–N distances and establish therefore that the crystallographic conformation is maintained in solution. Thus, the physical and chemical properties measured in solution do indeed reflect the stereochemistry of the single crystals. In addition, the introduction of only alkyl substituents to cause nonplanarity obviously circumvents potential electronic effects due to aryl ring interactions.

As has been observed for other distorted porphyrins,[4–6] NiTBuOEP exhibits red-shifted optical absorption spectra which are correctly predicted by semiempirical INDO/s calculations.[9] An additional assessment of the effects of the macrocycle distortion on the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals is obtained from cyclic voltammetry measurements of the first oxidation and reduction potentials which provide a complementary experimental probe of the migration of the frontier orbitals of the compound.[6,10]

Results and discussion

The title compound crystallizes quite easily from a variety of solvents. Nevertheless, crystals were frequently twinned and X-ray quality crystals were only obtained from mixtures of chlorinated solvents and hexane. A view of the molecular structure of NiTBuOEP crystallized from CH_2Cl_2–*n*-hexane is shown in Fig. 1. The compound crystallizes with half the molecule in the asymmetric unit and the nickel center located on a special position. The molecule is highly nonplanar and shows a ruffled[11] macrocycle conformation. This is evidenced by the large out-of-plane displacements of the meso carbon atoms, which are alternately displaced on average by 1.04 Å above and below the mean plane. The degree of ruffling and the in-plane rotation of the pyrrole rings (about the C_b–C_b axes) is shown in Figs. 2 and 3 and the average deviation of the macrocycle atoms from planarity (Δ24) is 0.462 Å. Averaged conformational parameters and geometrical data are compiled in Table 1.

The high degree of conformational distortion leads to very short metal–nitrogen bond lengths (Ni–N = 1.873(3) Å). This bond length is significantly shorter than those of ruffled[12a] (Ni–N = 1.929(3) Å, Δ24 = 0.26 Å) or planar[12b] (triclinic A modification; Ni–N = 1.958(2) Å, Δ24 = 0.02 Å) NiOEP[12] and NiTBuP[13] (Ni–N = 1.906(4) Å, Δ24 = 0.306 Å). This presents clear evidence that the high degree of ruffling observed in the title compound is not due to a simple small metal ion effect[14] but to the steric hindrance imposed at the porphyrin periphery by the presence of the meso- and β-alkyl substituents. In addition, the present structure provides further proof that meso-alkyl substituents in dodecasubstituted porphyrins induce selectively ruffling as the main distortion mode.[5a] For comparison, the structure of the highly saddle distorted (large C_b but no meso displacements), dodecasubstituted (2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) NiTPhOEP exhibits an average Ni–N bond length of 1.906(2) Å and a Δ24 of 0.62 Å.[6a] In contrast, the only other known nickel dodecaalkylporphyrin, $NiTPnTC_5P$ (see Chart 1), exhibits a ΔC_m of 0.8 Å, Δ24 of 0.39 Å and an average Ni–N bond length of 1.911(8) Å.[5a] Due to the small five-membered

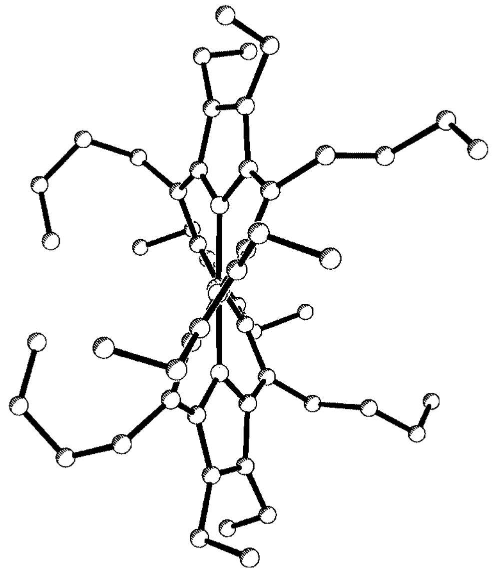

Fig. 2 Side view of the molecular structure of NiTBuOEP in the crystal. Hydrogen atoms and disordered positions have been omitted for clarity.

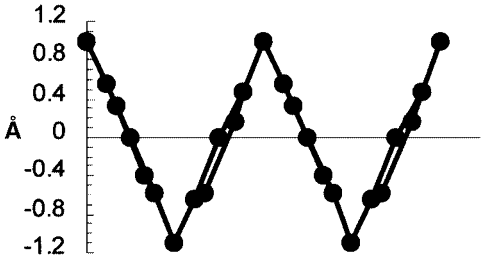

Fig. 3 View of the skeletal deviations of the 24 macrocycle atoms in NiTBuOEP from the least-squares plane of the four nitrogen atoms.

Table 1 Selected averaged bond lengths (Å), angles (°), and geometrical parameters (Å) for NiTBuOEP

Ni–N	1.873(3)	C_a–C_m	1.409(4)
N–C_a	1.375(4)	C_b–C_b	1.370(4)
C_a–C_b	1.453(4)		
N–Ni–N adjacent	90.00(11)	C_a–N–C_a	108.1(3)
N–Ni–N opposite	178.78(16)	C_a–C_m–C_a	119.2(3)
Ni–N–C_a	125.9(3)	C_a–C_b–C_b	107.1(3)
N–C_a–C_m	123.2(3)	C_m–C_a–C_b	127.3(3)
N–$C_a$$C_b$	108.8(3)	Pyr. tilt[a]	31.2
core size	1.872	ΔC_m[c]	1.044
Δ24[b]	0.462	ΔC_a[c]	0.562
ΔNi[c]	0.02	ΔC_b[c]	0.37
ΔN[c]	0.008		

[a] Angle between the pyrrole rings and the 4N-plane. [b] Average deviation of the 24 macrocycle atoms from their least-squares plane. [c] Deviations of geometrically equivalent positions from the 4N-plane.

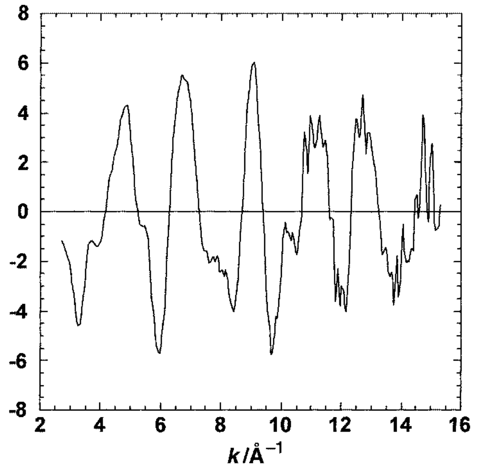

Fig. 4 Isolated k^3-weighted EXAFS oscillations for NiTBuOEP in toluene at room temperature.

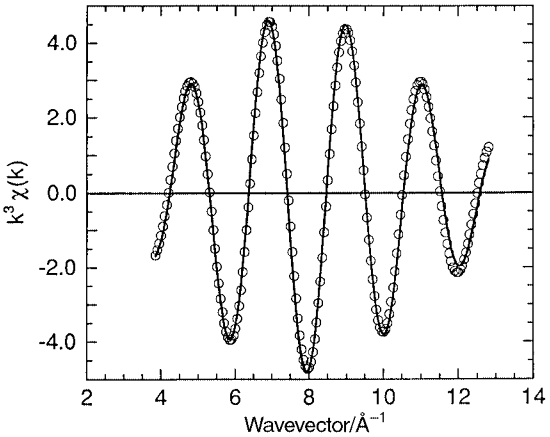

Fig. 5 Fourier-filtered first shell EXAFS oscillations (——) and nonlinear least-square fits (○) for NiTBuOEP in toluene at room temperature.

cyclopentenyl ring at the C_b positions, the C_b methylene groups are effectively removed from significant steric interactions with the meso pentyl chains (C_b–C_b–CH_2 angle = 112.4(9)°). This accounts for the significantly less distorted marcocycle in NiTPnTC$_5$P compared to NiTBuOEP. As in the present structure the C_b–C_b–CH_2 angles are 123.8(3)°, this gives further evidence for steric strain between the β-ethyl and meso butyl groups being the main cause of the observed nonplanarity.

No evidence was found for unusually short intermolecular macrocycle contacts in the crystal structure. The molecular structure is characterized by the porphyrin macrocycles being arranged in a layer-type structure with two of the four meso butyl chains pointing alternately up and down towards the next layer. In effect, the macrocycle atoms are separated by the interlocking "butyl arms" (not shown, but see Fig. 2). Thus, no packing effects on the porphyrins are evident in the crystal structure.

The isolated k^3-weighted EXAFS oscillations for NiTBuOEP are shown in Fig. 4. Fourier transform magnitudes of the k^3-weighted EXAFS data is shown in the supplementary material Fig. S2. Filtered first-shell EXAFS oscillations and the nonlinear least-squares fit is shown in Fig. 5. The fitting results are summarized in Table 2 (Table 1 in supplementary material). Analysis of the EXAFS data for NiTBuOEP in toluene at room temperature yields an average Ni–N distance of 1.87 Å (Fig. 4) in good agreement with the crystallographic average of 1.873(3) Å. The short Ni–N distances determined by EXAFS thus establishes that the nonplanarity of NiTBuOEP is maintained in solution and that the conformational distortion is an inherent property of the Ni complex and is not simply induced by crystal packing.

Table 2 Optical transitions and redox potentials

Compound	NiTBuOEP	NiOEP	NiTBuP
λ obsd^a/nm	632	550	576
E opt^b/eV	1.96	2.25	2.15
$\Delta E_{1/2}$^{c}/V	2.10	2.29	2.26
$E_{1/2}$(ox)^d/V	0.60	0.92	0.93
$E_{1/2}$(red)^d/V	−1.50	−1.37	−1.33

[a] Wavelength of the first optical trransition, measured in butyronitrile. [b] Energy of the first optical transition in butyronitrile (1240 nm = 1 eV). [c] $E_{1/2}$(ox) − $E_{1/2}$(red) in butyronitrile. [d] Half-wave potentials in butyronitrile with 0.1 M Bu_4NClO_4 *vs.* SCE.

A general consequence of the macrocycle distortions is that the optical transitions of the compounds are red-shifted compared to more planar molecules.[4–6] INDO/s calculations suggest that the effect is due to the destabilization of the porphyrin π system, with the HOMOs influenced more than the LUMOs. Therefore, the gap between the HOMOs and LUMOs is smaller, resulting in red-shifts of the optical spectra.[4–6,10b]

In the present case, the first optical transition of NiTBuOEP, which is a HOMO to LUMO excitation, occurs at 639 nm in toluene, 635 nm in CH_2Cl_2, and 632 nm in butyronitrile, significant bathochromic shifts relative to its "components", (2,3,7,8,12,13,17,18-octaethylporphyrinato)nickel(II) (NiOEP) and (5,10,15,20-tetrabutylporphyrinato)nickel(II) (NiTBuP) which absorb at 550 and 576 nm, respectively. INDO/s calculations of the low-energy optical band of NiTBuOEP, based on the crystallographic coordinates reported here, predict a transition at 667 nm, in reasonably good agreement (4–5%) with the experimentally observed values of 639–632 nm. (For comparison, the calculated value for the planar NiOEP agrees to ≈4%.) The theoretical calculations thus reinforce the conclusions reached above that the nonplanarity of NiTBuOEP is maintained in solution. Furthermore, the calculations also support the premise that it is indeed the macrocyclic distortion that causes the bathochromic optical shift. As well, since NiTBuOEP does not incorporate any aryl groups, the red-shifts observed clearly do *not* arise from any conjugation effects with aryl groups that are rotated into the porphyrin plane.

The redox potentials of porphyrins track the energy levels of the HOMOs and LUMOs of the complexes, and the differences between the first oxidation and reduction potentials, neglecting solvation effects, provide an indication of the energy of the first absorption band of porphyrins since this transition is principally a HOMO to LUMO excitation.[10]

The differences between the half wave potentials, ΔE, listed in Table 2, agree reasonably well with the energies of the first optical transitions (the maximum deviation between the redox and optical data is ≈7%), and thus support the notion that the redox potentials reflect the relative energies of the HOMOs and LUMOs in both planar and nonplanar macrocycles. The presence of a 1s–4p$_z$ peak in the XANES spectrum of NiTBuOEP indicates that the nickel remains four coordinate in solution, see supplementary material Fig. S1.

Although NiTBuOEP is basically a hybrid of NiOEP and NiTBuP, the compound is significantly easier to oxidize than either of its "constituents" (Table 2), by 0.32 and 0.33 V, respectively, in agreement with the theoretically predicted destabilization of the HOMO due to the conformational distortion. In contrast, the reduction potential of NiTBuOEP shifts by 0.13 and 0.17 V compared to those of NiOEP and NiTBuP, respectively, and thus also follows the trend observed in other nonplanar porphyrins that the LUMO into which the electron is added is less sensitive to macrocyclic distortions than the

HOMO, resulting in a smaller gap between the two orbitals and thereby causing the observed optical red shifts.

Conclusions

Crystallographic results establish that NiTBuOEP adopts a nonplanar, ruffled conformation with short Ni–N distances. EXAFS results yield identical Ni–N values in solution and thus confirm that the distorted conformation is retained in solution. The compound exhibits significantly red-shifted optical transitions correctly predicted by INDO/s calculations. The bathochromic shifts are attributed to a predominant destabilization of the HOMO, an effect also reflected by its electrochemical oxidation potential. These modulations are best assigned to the conformational distortion rather than to substituent electronic interactions.

Experimental

NiTBuOEP was prepared by direct alkylation of NiOEP with butyl lithium as described recently.[8] Optical spectra were recorded on a Cary 500 spectrophotometer: λ_{max} in toluene: 461, 592 and 639 nm; in CH_2Cl_2: 459, 590 and 635 nm, in butyronitrile: 458, 590 and 632 nm. Redox potentials were determined by cyclic voltammetry in butyronitrile with 0.1 M Bu_4NClO_4 as supporting electrolyte on a BAS 100A electrochemical analyzer. Solvents were dried and distilled immediately before use. Optical spectra were calculated with the INDO/s (intermediate neglect of differential overlap) method developed by Zerner and co-workers for optical spectra of porphyrins.[9] The method consists of a ground-state self-consistent field calculation followed by monoexcited configuration interaction. Excitations were generated from an active space comprised of 11 HOMOs and 11 LUMOs. The coordinates reported here were used in the calculations.

X-Ray absorption experiments were performed at the Brookhaven National Synchrotron Light Source on beamline X-19A. Data were collected with Si 311 (X-19A) monochromator crystals with slits adjusted to give ≈1–2 eV resolutions. The samples were measured in fluorescence mode with a Canberra 13-element detector. The sample was measured as a solution in toluene-d_8 using previously published EXAFS cells.[15] Data were collected in ≈20 minute scans yielding $>10^6$ counts of signal at the nickel K-edge for each sample. Energies were calibrated against a nickel foil (8333 eV) which was present throughout the data collection. The data were analyzed using the MacXAFS EXAFS analysis package.[16] The EXAFS oscillations for the samples and standard were isolated using standard methods: linear extrapolation and subtraction of a pre-edge bulk-absorption contribution, normalization of the edge step, interpolation onto a photoelectron momentum (k) grid, and removal of a smooth background with a series of three cubic splines. E_0 was defined as the energy corresponding to the midpoint of the main absorption step. The resulting oscillations were weighted with k^3 factors and Fourier-filtered to isolate first-shell contributions as amplitude and phase functions. Quantitative comparisons between unknowns and standards were accomplished with nonlinear fits based on the general EXAFS equation.[17] Ni(II)porphycene was used as an experimental standard (Ni–N distance = 1.89 Å).[18] Theoretical standards were generated using FEFF 6.01, an *ab initio*, curved-wave, multiple scattering EXAFS simulation code.[19,20]

Crystal structure determination of NiTBuOEP

X-Ray quality crystals were grown by liquid diffusion from CH_2Cl_2–*n*-hexane. 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] When using oil techniques for crystal mounting, care has to be taken since crystals of this compound are prone to dissolve in nonpolar solvents. Intensity data were collected with an Syntex $P2_1$ instrument using graphite filtered Cu-K_α radiation ($\lambda = 1.54178$ Å) at 126 K with 2θ–θ scans. An absorption correction was applied using the program XABS2,[22] while extinction effects were disregarded. The structure was solved with a Patterson synthesis followed by structure expansion with the program SHELXS-93.[23] Refinements were carried out by full-matrix least-squares on $|F^2|$ using the program SHELXL-97.[24]

The methyl group of the 10-butyl chain was disordered and refined with two split positions. Occupancies were determined by free refinement to be C104 0.65 and C10d 0.35. Despite restraining the bond length the C103 C10D bond length remained at an unreasonably short value. All nonhydrogen atoms were refined with anisotropic thermal parameters.

Crystal data for NiTBuOEP

$C_{52}H_{76}N_4Ni$, MW = 815.88, green block, monoclinic, space group *C2/c*, $a = 26.581(11)$ Å, $b = 7.566(2)$ Å, $c = 25.967(12)$ Å, $\beta = 119.62(3)°$, $V = 4540(3)$ Å^3, $Z = 4$, $D_{calc} = 1.194$ Mg m^{-3}, $\mu = 0.897$ mm^{-1} (T_{max}, $T_{min} = 0.62, 0.62$), $\theta_{max} = 57.08°$, 3431 reflections collected, 3058 independent reflections, $R_{int} = 0.1080$, $\Delta/\rho_{max} = 0.526$ e Å^{-3}, $R1$ [$F > 4.0\sigma(F)$] = 0.0552, $wR2$ [$F > 4.0\sigma(F)$] = 0.1430, $R1$ (all data) = 0.0603, $wR2$ (all data) = 0.1469.

CCDC reference number 186/1770.

See http://www.rsc.org/suppdata/dt/a9/a905927j/ for crystallographic files in .cif format.

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References

1 S. M. Prince, M. Z. Papiz, A. A. Freer, G. McDermott, A. M. Hawthornthwaite-Lawless, R. J. Cogdell and N. W. Isaacs, *J. Mol. Biol.*, 1997, **268**, 412; S. M. Prince, Y.-F. Li, W. Zhou, R. E. Blankenship and J. P. Allen, *J. Mol. Biol.*, 1997, **271**, 456.

2 V. Ermler, G. Fritch, S. K. Buchanan and H. Michel, *Structure*, 1994, **2**, 925; J. Deisenhofer, O. Epp, I. Sinning and H. Michel, *J. Mol. Biol.*, 1995, **246**, 429.

3 M. Sundaramoorthy, K. Kishi, M. H. Gold and T. L. Poulos, *J. Biol. Chem.*, 1994, **269**, 32759; K. G. Ravichandran, S. S. Boddupalli, C. A. Hasemann, J. A. Peterson and J. Deisenhofer, *Science*, 1993, **261**, 731; B. R. Crane, L. M. Siegel and E. D. Getzoff, *Science*, 1995, **270**, 59; M. J. Maté, M. Zamocky, L. M. Nykyri, C. Herzog, P. M. Alzari, C. Betzel, F. Koller and I. Fita, *J. Mol. Biol.*, 1999, **268**, 135.

4 (*a*) W. Jentzen, X. Z. Song and J. A. Shelnutt, *J. Phys. Chem.*, 1997, **101**, 1684; J. D. Hobbs and J. A. Shelnutt, *J. Protein Chem.*, 1995, **14**, 19; (*b*) Reviews: A. Forman, M. W. Renner, E. Fujita, K. M. Barkigia, M. C. W. Evans, K. M. Smith and J. Fajer, *Isr. J. Chem.*, 1989, **29**, 57; R. Huber, *Eur. J. Biochem.*, 1990, **187**, 283; J. Fajer, *Chem. Ind.* (*London*), 1991, 869; M. O. Senge, *J. Photochem. Photobiol. B: Biol.*, 1992, **16**, 3; M. Ravikanth and T. K. Chandrashekar, *Struct. Bonding* (*Berlin*), 1995, **82**, 105; J. A. Shelnutt, X.-Z. Song, J.-G. Ma, S.-L. Jia, W. Jentzen and C. J. Medforth, *Chem. Soc. Rev.*, 1998, **27**, 31; M. O. Senge, in *Handbook of Porphyrins*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, New York, 2000, ch. 6.

5 (*a*) C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1992, **114**, 9859; (*b*) S. Gentemann, C. J. Medforth, T. P. Forsyth, D. J. Nurco, K. M. Smith, J. Fajer and D. Holten, *J. Am. Chem. Soc.*, 1994, **116**, 7363; A. Regev, T. Galili,

C. J. Medforth, K. M. Smith, K. M. Barkigia, J. Fajer and H. Levanon, *J. Phys. Chem.*, 1994, **98**, 2520; M. W. Renner, K. M. Barkigia, Y. Zhang, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1994, **116**, 8582; M. O. Senge, T. P. Forsyth, L. T. Nguyen and K. M. Smith, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2485; P. Ochsenbein, K. Ayougou, D. Mandon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Terner and J. Fajer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 348; J. Takedo and M. Sato, *Chem. Lett.*, 1995, 939; J. A. Hodge, M. G. Hill and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 809; S. Gentemann, S. H. Leung, K. M. Smith, J. Fajer and D. Holten, *J. Phys. Chem.*, 1995, **99**, 4330; S. Gentemann, C. J. Medforth, T. Ema, N. Y. Nelson, K. M. Smith, J. Fajer and D. Holten, *Chem. Phys. Lett.*, 1995, **245**, 441; C. M. Drain, C. Kirmaier, C. J. Medforth, D. J. Nurco, K. M. Smith and D. Holten, *J. Phys. Chem.*, 1996, **100**, 11984; P. Tagliatesta, J. Li, M. Autret, E. Van Caemelbecke, A. Villard, F. D'Souza and K. M. Kadish, *Inorg. Chem.*, 1996, **35**, 5570; D. J. Nurco, C. J. Medforth, T. P. Forsyth, M. M. Olmstead and K. M. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 10918; M. O. Senge and W. W. Kalisch, *Inorg. Chem.*, 1997, **36**, 6103; S. Gentemann, N. Y. Nelson, L. Jaquinod, D. J. Nurco, S. H. Leung, C. J. Medforth, K. M. Smith, J. Fajer and D. Holten, *J. Phys. Chem. B*, 1997, **101**, 1247; M. W. Renner, K. M. Barkigia and J. Fajer, *Inorg. Chim. Acta*, 1997, **263**, 181.

6 (*a*) K. M. Barkigia, M. W. Renner, L. R. Furenlid, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1993, **115**, 3627; (*b*) K. M. Barkigia, D. J. Nurco, M. W. Renner, D. Melamed, K. M. Smith and J. Fajer, *J. Phys. Chem. B*, 1998, **102**, 322.

7 A. Stone and A. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735; J. L. Hoard, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975, p. 317; S. G. DiMagno, A. K. Wertshing and C. R. Ross, *J. Am. Chem. Soc.*, 1995, **117**, 8279.

8 W. W. Kalisch and M. O. Senge, *Angew. Chem., Int. Ed.*, 1998, **37**, 1107.

9 J. Ridley and M. Zerner, *Theor. Chim. Acta* (*Berlin*), 1973, **32**, 111; 1976, **42**, 223; M. Zerner, G. Loew, R. Kirchner and U. Mueller-Westerhoff, *J. Am. Chem. Soc.*, 1980, **102**, 589.

10 (*a*) R. H. Felton, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 5, p. 53; (*b*) K. M. Barkigia, L. Chantranupong, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1988, **110**, 7566.

11 Y. J. Lee and W. R. Scheidt, *Struct. Bonding* (*Berlin*), 1987, **64**, 1.

12 (*a*) E. F. Meyer Jr., *Acta Crystallogr., Sect. B*, 1972, **28**, 2162; (*b*) D. L. Cullen and E. F. Meyer Jr., *J. Am. Chem. Soc.*, 1974, **96**, 2095.

13 M. W. Renner, J. Fajer and M. O. Senge, unpublished work.

14 J. L. Hoard, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 18.

15 L. R. Furenlid, M. W. Renner and J. Fajer, *Rev. Sci. Instrum.*, 1990, **61**, 1326.

16 C. E. Bouldin, W. T. Elam and L. Furenlid, *Physica B*, 1995, **208/209**, 739.

17 (*a*) E. A. Stern and S. M. Heald, in *Handbook on Synchrotron Radiation*, eds. E. A. Stern and S. M. Heald, Springer-Verlag, Amsterdam, 1983; (*b*) B. K. Teo, in *EXAFS: Basic Principles and Data Analysis*, ed. B. K. Teo, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1986.

18 L. R. Furenlid, M. W. Renner, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1990, **112**, 1634.

19 J. Mustre de Leon, J. J. Rehr and S. I. Zabinsky, *Phys. Rev. B*, 1991, **44**, 4146.

20 J. J. Rehr, M. Balci, K. Pramod, P. Koch, J. Lex and O. Ermer, *J. Am. Chem. Soc.*, 1991, **113**, 5135.

21 H. Hope, *Prog. Inorg. Chem.*, 1994, **41**, 1.

22 S. R. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.

23 G. M. Sheldrick, SHELXS-93, Program for Crystal Structure Solution, Universität Göttingen, Germany, 1993.

24 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.

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