

Axial Coordination Phenomena in Highly Substituted Porphyrins. Crystal Structure of the Polymeric (2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetranitroporphyrinato)zinc(II), $[\{Zn(oetnp)\}_n]$

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The polymeric structure of the sterically strained and non-planar porphyrin $[\{Zn^{\text{II}}oetnp\}_n]$ is determined by X-ray crystallography; polymerization is achieved by utilization of the nitro-groups for axial ligation to the zinc(II) centre.

Highly substituted porphyrins^{1a} are of considerable interest for mimicking the influence of the macrocycle conformation on the metalloporphyrin properties in porphyrin-protein complexes.^{1b} Dodecasubstituted porphyrins have been shown to exhibit a variety of different macrocycle conformations with severely non-planar ring systems.^{1b,2} The porphyrin H_2oetnp has also been shown to have a severely distorted macrocycle, the specific conformation in metal complexes being dependent on the central metal.³ During studies on the axial coordination of different bases to the zinc(II) complex, $[Zn(oetnp)]$, prepared following the standard procedure,⁴ we obtained crystalline material of $[\{Zn(oetnp)\}_n]$ which displays a remarkable polymer structure involving ligation of nitro-groups to the zinc centre.

The crystal structure of $[\{Zn(oetnp)\}_n]^\dagger$ revealed the formation of an extended two-dimensional network of porphyrin macrocycles interconnected by ligation of nitro groups to the zinc centre. The bond length of the connecting $Zn(1)-O(9)$ group is 2.485(5) Å. The compound crystallizes with two macrocycles per asymmetric unit, as shown in Fig. 1. The two neighbouring macrocycles are almost orthogonal to each other, the angle between the two four-nitrogen atom planes (4N-plane) being 86.8°. The polymeric structure of this compound is shown in Fig. 2. It is characterized by a zigzag arrangement of the macrocycles. The parallel chains are related by $Zn \cdots Zn$ distances of 8.03 Å for neighbouring molecules with '—|' orientation and of 10.93 Å for neighbour-

ing centres with '—|' orientation. In addition to the bonds between Zn and the nitro oxygen which make up the polymer chains, there are other close contacts between the Zn atom and NO_2 -groups on the side opposite the short axial Zn-O bond. These distances are: $Zn(1)-O(14)$ 3.185, $Zn(1)-O(13)$ 3.78, $Zn(2)-O(3)$ 3.274 and $Zn(2)-O(4)$ 3.568 Å. These contacts connect the polymer chain with the next ones above and below. The parallel running polymer chains are very weakly connected by interaction between an ethyl hydrogen and a nitro oxygen atom (2.578 Å) and are characterized by a separation of the Zn-axes of 13.138 Å. To a certain degree the structure can therefore be described as a network of polymers.

Two other polymeric structures are known which involve a

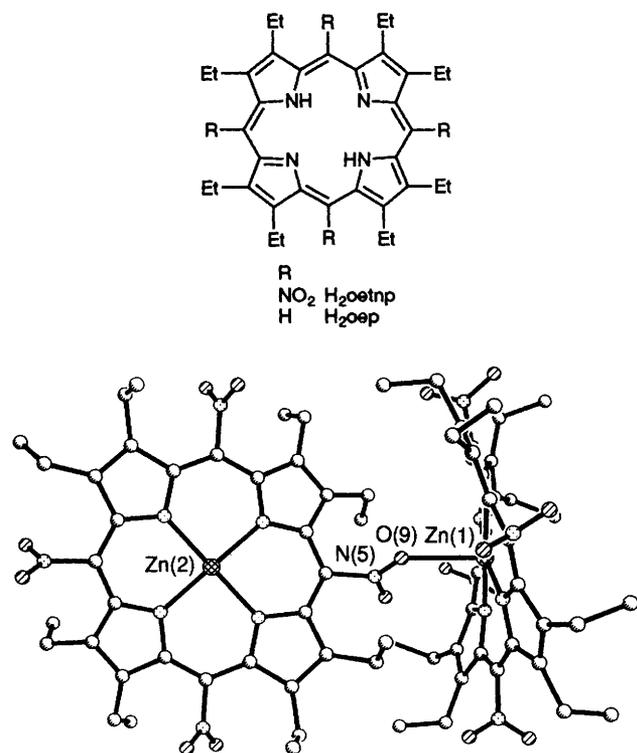


Fig. 1 Computer generated plot of the two $[Zn(oetnp)]$ macrocycles in the asymmetric unit. Disordered positions and hydrogen atoms have been omitted for clarity.

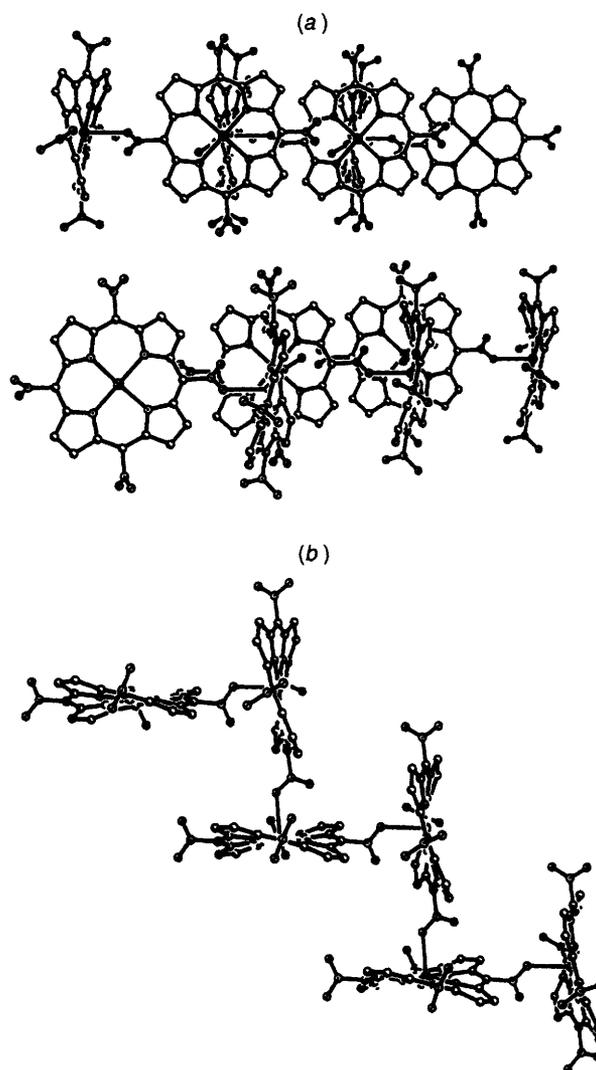


Fig. 2 Views of the molecular arrangement in the crystal. View (a) shows the parallel arrangement of the polymer chains and (b) shows a side view of one of the polymers. All hydrogen atoms and side-chain ethyl groups have been omitted for clarity.

porphyrin substituent functioning as axial ligand.⁵ However, these involve pyridine functionalities, which are known to bind strongly to zinc(II) porphyrins. In the present case, the presence of *one* nitro group alone does not lead to polymer formation. This is evidenced by the fact that the corresponding derivatives with one, [Zn(5-NO₂-oep)],⁶ or two nitro groups [Zn{5,15-(NO₂)₂-oep}]⁷ do not form such polymers. Instead they form closely packed lattices with parallel orientation of the macrocycle planes. In the former case the molecules additionally form π -stacked dimers.⁶ Such close packing is not possible in the case of the tetranitro derivative [Zn(oetnp)] due to steric repulsion resulting from the ring deformation. Due to the same reason we have so far been unable to co-crystallize or form solution complexes with π acceptors like fluorenone or tetracyanoquinodimethene derivatives. Thus, the formation of the polymeric form depends on two factors: the inability to pack the molecules in a closely spaced, parallel fashion and the presence of *four meso*-nitro groups making the zinc metal so electron deficient that it accepts a nitro group as axial ligand.‡

The metal-axial ligand bond length is 2.485 Å; this is longer than the Zn-O distances observed *e.g.* in zinc(II) porphyrins with methanol as axial ligand [≈ 2.2 Å].^{2a,5,7} The nitro group binds in a monodentate fashion, the Zn-O distance to the other oxygen atom of the ligating nitro group is 3.443 Å. The zinc atoms are displaced by 0.12 Å from the 4N-planes. The Zn-N_p bond lengths are 2.047(4) Å and the N-Zn-N bond angles are 89.9(2)°. These values are comparable with values found in other zinc(II) porphyrins,^{7,8} while the geometrical features of the ligand system are characteristic for a non-planar porphyrin structure.²

The macrocycles are clearly non-planar (Figs. 1 and 2). This is evidenced by an average displacement of the 24 core atoms from their mean plane by 0.38 Å. The C_b-atoms are displaced by 0.78 Å from the plane of the four nitrogens. This distortion is less than that observed in dodecaalkyl/arylporphyrins² or [(Ni(oetnp))]^{3b} but comparable with that observed in the free base, H₂oetnp.^{3b} The two macrocycles in the asymmetric unit differ slightly in their conformation. While the C_m-atoms in the macrocycle containing Zn(1) are clearly displaced from the 4N-plane by 0.1 Å, the C_m-atoms in the macrocycle containing Zn(2) are almost in plane (average deviation 0.03 Å). Overall, the conformation can best be described by the typical saddle conformation observed in other dodecasubstituted porphyrins,² with alternating displacement of the pyrrole rings below and above the mean plane. Due to this saddle conformation the ligating nitro-group and part of the neighbouring porphyrin sits end on in the cavity formed by the side chains of the distorted macrocycle. This glove-like fit may be the reason for the preference of nitro group coordination over methanol.

The situation in solution was studied by absorption spectroscopy. UV-VIS spectra in methylene chloride exhibited maxima at 424, 558 and 588 nm (432 and 566 nm in chloroform). Addition of 1% methanol to the CH₂Cl₂ solution gave a slight red shift to 432 and 566 nm while a solution in CH₂Cl₂ containing 1% pyridine gave a strong bathochromic shift (446 and 578 nm) indicating ligation of the pyridine to the Zn^{II} centre, thus preventing polymer formation. The formation of monomeric species was confirmed by spectroscopic and crystallographic studies on the co-ordination of strong bases to [Zn(oetnp)]. In all cases studied so far (pyridine and imidazole

derivatives) monomeric, five coordinated species were obtained. The results of our studies on the different (monomeric) axial ligand complexes will be reported in due course.

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Footnotes

† Crystal data for {[Zn(oetnp)]_n}: black parallelepipeds from CHCl₃-MeOH (containing 1% pyrrole); [C₃₆H₄₀N₈O₈Zn]_n, triclinic, *P*1; *Z* = 4 (2 porphyrins per asymmetric unit), 126 K, λ (Cu-K α) = 1.54178 Å, *a* = 10.934(2), *b* = 12.443(3), *c* = 27.012(5) Å, α = 79.41(2), β = 84.47(2), γ = 89.60(2)°, *U* = 3581(1) Å³; 7229 observed reflections with *F* > 4.0 σ (*F*); *F*(000) = 1624, μ = 1.493 mm⁻¹; except for the disordered positions, all non-hydrogen atoms were refined with anisotropic thermal parameters; *R* = 0.089. One ethyl group disordered over two split positions, high thermal motion observed for two ethyl and one nitro group. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Note that [Zn(5-NO₂-oep)] in the presence of methanol crystallizes as the methanol solvate,^{6b} while {[Zn(oetnp)]_n} was crystallized also in the presence of methanol but instead utilizes the nitro groups as axial ligands.

References

- (a) J.-H. Fuhrhop, L. Witte and W. S. Sheldrick, *Liebigs Ann. Chem.*, 1976, 1537; (b) K. M. Barkigia, L. Chantranupong, K. M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 1988, **110**, 7566.
- (a) K. M. Barkigia, M. D. Berber, J. Fajer, C. J. Medforth, M. W. Renner and K. M. Smith, *J. Am. Chem. Soc.*, 1990, **112**, 8851; (b) C. J. Medforth, M. O. Senge, K. M. Smith, L. D. Sparks and J. A. Shelnutz, *J. Am. Chem. Soc.*, 1992, **114**, 9859; L. D. Sparks, C. J. Medforth, M.-S. Park, J. R. Chamberlain, M. R. Ondrias, M. O. Senge, K. M. Smith and J. A. Shelnutz, *J. Am. Chem. Soc.*, 1993, **115**, 581; 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; (c) D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayarai, R. N. Austin, A. Gold, P. S. White, O. Brigaud, P. Battioni and D. Mansuy, *Inorg. Chem.*, 1992, **31**, 2044; (d) P. Bhyrappa, V. Krishnan and M. Nethaji, *J. Chem. Soc., Dalton Trans.*, 1993, 1901.
- (a) J. A. Shelnutz, S. A. Majumder, L. D. Sparks, J. D. Hobbs, C. J. Medforth, M. O. Senge, K. M. Smith, M. Miura, L. Luo and J. M. E. Quirke, *J. Raman Spectrosc.*, 1992, **23**, 523; (b) M. O. Senge, *J. Chem. Soc., Dalton Trans.*, 1993, 3539.
- E. Watanabe, S. Nishimura and H. Ogoshi, *Tetrahedron*, 1975, **31**, 1385.
- M. J. Gunter, G. M. McLaughlin, K. J. Bery, K. S. Murray, M. Irving and P. E. Clark, *Inorg. Chem.*, 1984, **23**, 283; A. M. Shachter, E. B. Fleischer and R. C. Haltiwanger, *J. Chem. Soc., Chem. Commun.*, 1988, 960.
- (a) R. J. Abraham, B. Evans and K. M. Smith, *Tetrahedron*, 1978, **34**, 1213; (b) M. O. Senge, C. W. Eigenbrot, T. D. Brennan, J. Shusta, W. R. Scheidt and K. M. Smith, *Inorg. Chem.*, 1993, **32**, 3134.
- N.-J. Zhu, Y. Li, G.-Z. Wu and X.-G. Liang, *Acta Chim. Sin.*, 1992, **50**, 249.
- W. R. Scheidt and Y. L. Lee, *Struct. Bonding (Berlin)*, 1987, **64**, 1.