Characterization of a 5-Pyridyl-10,15,20-triphenylporphyrinatozinc(II) Polymer

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The long chain structure of a polymer of 5-pyridyl-10,15,20-triphenylporphyrinatozinc(II) was determined by u.v.–visible spectroscopy, proton n.m.r., and *X*-ray crystallography.

We report the synthesis, spectroscopic characterization, and crystal structure of a polymer of 5-pyridyl-10,15,20-triphenylporphyrinatozinc(II), the polymeric linkage which is formed by ligation of a pyridine nucleus on the porphyrin periphery to the zinc metal centre of an adjacent metalloporphyrin molecule. This represents one of the few crystal structure characterizations of a porphyrin polymer system in which a substituent on the porphyrin ring participates in the polymeric linkage.[1]

The monomeric porphyrin unit was prepared according to literature methods.[2] Pyrrole, benzaldehyde, and pyridine-4-carbaldehyde were refluxed in propionic acid for 1 h. The mixture was then cooled and filtered. The purple crystalline product was washed with methanol. The product was then purified and the six isomers were separated by thin-layer and column chromatography. The pure monopyridyl product† was then metallated with zinc acetate in dimethylformamide. The purple product was crystallized from dichloromethane–methanol.

The polymer was characterized by u.v.–visible and ^{1}H n.m.r. spectroscopy, and *X*-ray crystallography. In solution, the u.v.–visible spectra showed the ligation of pyridine to the zinc porphyrin: α and β bands had undergone a bathochromic shift, as in the case of pyridine ligation to zinc tetraphenylporphyrin in chloroform (556 to 560 nm and 596 to 602 nm). Additionally, as the concentration was increased a slightly greater bathochromic shift was observed (560 to 562 nm and 602 to 606 nm) perhaps due to increased polymer length.

A model was derived in which it was assumed that the build-up of the polymer could be described by one statistical equilibrium constant; a good fit to the extinction coefficient dependence of the 5-pyridyl-10,15,20-triphenylporphyrinato-zinc(II) concentration indicated that the solution behaviour could be described in terms of the polymer formation. The extinction coefficient at 602 nm increased from 3200 l mol^{-1} cm^{-1} at a porphyrin concentration of 1×10^{-6} M to 8500 l mol^{-1} cm^{-1} for a 2.5×10^{-3} M-solution.

The ^{1}H n.m.r. data also indicated that the pyridine on the porphyrin ring was bound to the zinc centre of another porphyrin molecule. The signals of the pyridine protons in

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† Satisfactory elemental analyses were obtained.

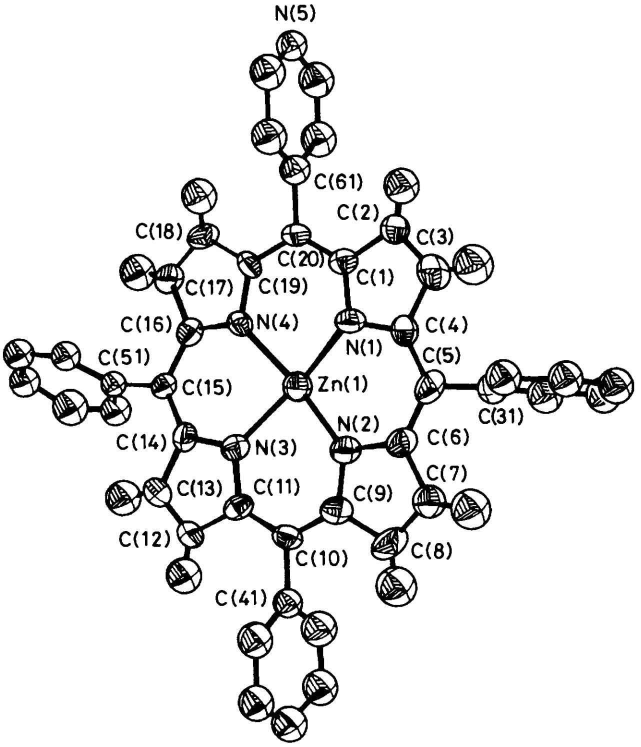

Figure 1. ORTEP plot of 5-pyridyl-10,15,20-triphenylporphyrinatozinc(II) (the phenyl hydrogen atoms have been deleted for clarity).

deuteriochloroform occurred at δ 6.2 and 2.6 and those of the pyrrole β-protons at 7.4, 8.5, and 8.8 (in tetraphenylporphyrin these pyrrole protons give a singlet at δ 8.75). These shifts indicate that the protons are in the ring current of the porphyrin to which the pyridine is bound. A similar high-field shift was observed in the proton n.m.r. of pyridine bound to tetraphenylporphinatozinc(II):[3] the pyridine signals occurred at 2.66, 5.50, and 6.34 (unbound pyridine 8.58, 7.21, and 7.62).

The precise structure of the polymer was determined by *X*-ray crystallography.‡ An ORTEP drawing of the monomer appears in Figure 1. The crystal structure revealed that the polymer is in a long-chain, zig-zag conformation (Figure 2). the zinc–pyridine bond (2.234 Å) is slightly longer than similar zinc–pyridine bonds (2.0—2.2 Å) in other porphyrin structures.[4]

Moreover, the zinc–pyridine bond is not perpendicular to the porphyrin plane, but is tilted 10° from the normal position. This has been observed in several other zinc–pyridine porphyrin structures, but not to the present extent.[5] Furthermore, the pyridine ring is tipped with respect to the Zn–N(py) bond; that is, the plane of the pyridine ring and the Zn–N(py) bond form an angle of 155.6 (8)° rather than the expected 180°. This deviation is unusual for pyridine–porphyrin complexes.[4]

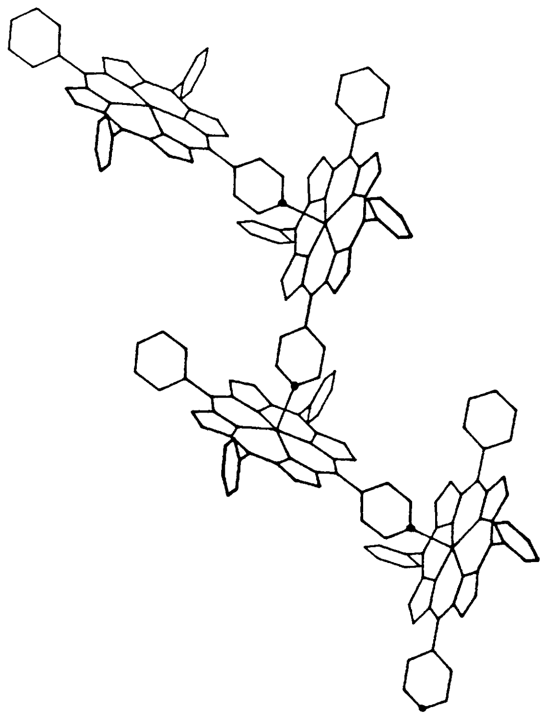

Figure 2. Polymer conformation.

Additionally, the zinc is 0.28 Å out of the porphyrin plane, a distance similar to that found in other zinc porphyrins (0.2—0.3 Å).[4] The plane of the porphyrin displays some displacement of the pyrrole carbon atoms; deviations from the nitrogen plane range from 0.00(3) to 0.22(7) Å. The bond lengths and angles of the porphyrin monomer are similar to those of other porphyrin structures.[6] The Zn–N bond lengths are 2.069(6), 2.066(6), 2.070(6), and 2.053(6) Å, and the N–Zn–N bond angles 88.5(2)°, 89.3(2)°, 89.6(2)°, and 88.3(2)°. The carbon–carbon and carbon–nitrogen bond lengths and angles are as expected.§

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References

1 M. J. Gunter, G. M. McLaughlin, K. J. Berry, K. S. Murray, M. Irving, and P. E. Clark, *Inorg. Chem.*, 1984, **23**, 283.

2 E. B. Fleischer, *Inorg. Chem.*, 1968, **1**, 493; A. Aldler, F. R. Longo, F. Kampos, and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443; C. Franco and G. McLendon, *Inorg. Chem.*, 1984, **23**, 2370.

3 C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, 1969, **8**, 2141.

4 D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, 1970, **92**, 3761; G. Margui, M. Cammas, and G. Carta, *J. Coord. Chem.*, 1973, **2**, 167; G. J. B. Williams, L. C. Andrews, and L. D. Spaulding, *J. Am. Chem. Soc.*, 1977, **99**, 6918; D. L. Cullen and E. F. Meyer, *Acta Crystallogr., Ser. B*, 1976, **32**, 2259.

5 G. J. B. Williams, L. C. Andrews, and L. D. Spaulding, *J. Am. Chem. Soc.*, 1977, **99**, 6918; D. L. Cullen and E. F. Meyer, *Acta Crystallogr., Sect. B*, 1976, **32**, 2259.

6 R. W. Scheidt, 'The Porphyrins,' Vol. 4, ed. D. Dolphin, Academic Press, New York, 1978, ch. 10.

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‡ The purple plates of $(C_{43}H_{27}N_5Zn)_n$ crystallized in the monoclinic space group $P2_1/c$ with a = 10.8392(3), b = 19.1240(9), c = 16.1580(6) Å, β = 90.326 (3)°, V = 3348.16(2) Å^3, D_c = 1.35 g cm^{-3}, μ = 7.86 cm^{-1}, Z = 4 at 298 K. Data were collected with a Syntex P3/F diffractometer, with Mo-K_α radiation. The structure was solved using Patterson and Fourier methods and refined by blocked cascade diagonal least-squares calculations. Positional and anisotropic parameters were refined for all non-H atoms. For 322 parameters, $F > 6\sigma(F)$, and 2130 observed reflections, the refinement yielded R = 0.0626. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

§ We have also prepared the dipyridyldiphenylporphyrins (both *cis*-5,10- and the *trans*-5,15-dipyridyl); apparently they form two- and three-dimensional metalloporphyrin polymer systems, which are being studied.