Tetrahedron Letters, Vol. 33, No. 45, pp. 6871-6874, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

STRUCTURES OF THE ZINC COMPLEXES OF THE BILINONES FORMED BY PHOTO-OXIDATIONS OF *MESO*-TETRAPHENYLPORPHYRINS

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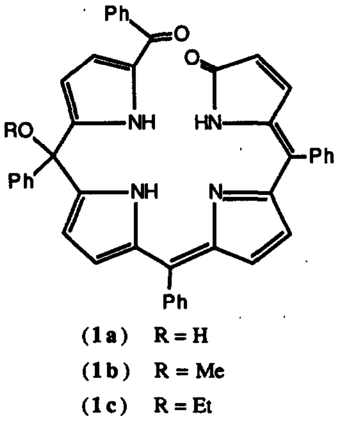
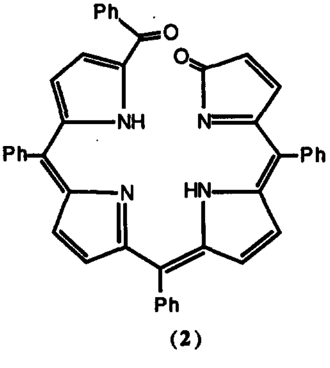
Abstract: The ring-opened bilinones formed by photo-oxidation of *meso*-tetraphenylporphyrins and their metal complexes form yellow-brown and blue zinc complexes, the structures of which were deduced from extensive n.m.r. studies.

In earlier studies[1] we showed that photo-oxidations of *meso*-tetraphenylporphyrin (TPP) dianions in water or alcohol solvents afford ring-opened violet bilinones of general structure (1). Similar products had been obtained by photo-oxidation of group II metal complexes of TPP followed by removal of the metal,[2,3] from oxidation of metal complexes of TPP with thallium(III) or cerium(IV) salts,[4] from the cation-radical of TPP metal complexes[5], and from a zinc isoporphyrin derivative.[6] An incorrect structure had been assigned originally to these materials but our extensive n.m.r. studies, the preparation and n.m.r. studies of *meso*-^{13}C-labelled analogues, and careful field desorption mass spectral measurements enabled us to deduce[1] the correct structure (1). The formation of the *meso*-substituted bilinones (1) rather than the fully conjugated biliverdin type of structure (2) was attributed to relief of steric hindrance in the latter by addition of water, methanol or ethanol at a *meso* bridge position.



(1a) R = H
(1b) R = Me
(1c) R = Et



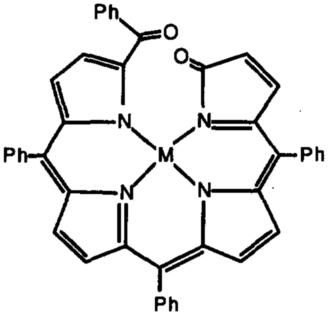
(2)

The primary products from the photo-oxidation of TPP metal complexes are thought[3] to have the structure (**3**), and it is only during removal of the metal by addition of acidified hydroxylic solvents that addition of water, or an alcohol, occurs to give the violet pigments (**1**). For this reason and because there has been considerable interest[7] in the structures of metal complexes of bile pigments, we considered it important to investigate more thoroughly the metal complexes formed by the bilinones (**1**).

Addition of zinc acetate in methanol to a chloroform solution of the methanol adduct (**1b**) immediately afforded a yellow brown complex (**A**) ($\lambda_{max.}$ 825 nm) whereas under the same conditions the water adduct (**1a**) gave a bright blue complex (**B**) ($\lambda_{max.}$ 624 nm). Subsequently, we discovered that on standing in chloroform for a few days the yellow brown complex (**A**) was slowly transformed into a blue complex which appeared to be identical (visible, n.m.r. and mass spectrometry) with the blue complex (**B**) formed directly from the water adduct (**1a**). Conversely on heating the solution, the blue complex (**B**) was transformed into a yellow brown material with the same visible spectrum as complex (**A**).

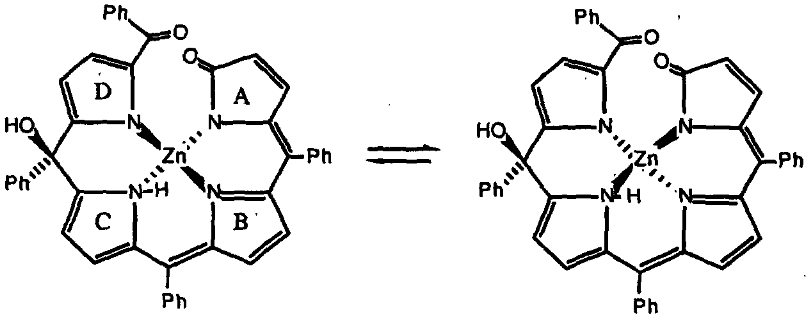
$$\begin{tikzcd}
(\mathbf{1a}) \arrow[r, "Zn(OAc)_2"] & \text{blue } (\mathbf{B}) \arrow[d, shift right, "\text{heat}"'] \\
(\mathbf{1b}) \arrow[r, "Zn(OAc)_2"] & \text{yellow brown } (\mathbf{A}) \arrow[u, shift right, "\text{stand in solution}"']
\end{tikzcd}$$

The yellow brown zinc complex (**A**) was assigned the structure (**3**, M=Zn) on the basis of visible, n.m.r.[9] and mass spectra and the similarity of the visible spectra with those of the intermediate (**3**, M=Cd) formed in the photo-oxidation of the cadmium complex of TPP[3] and the zinc complex of a corresponding formylbilinone derived from octaethylporphyrin.[8] The ^{13}C n.m.r. spectrum was also consistent with the fully conjugated structure (**3**, M=Zn), the *meso*-^{13}C material showing resonances at 116.8, 135.0, 148.9 and 187.4 p.p.m.. The coordination around the zinc atom is expected to be tetrahedrally distorted from planarity.



(**3**)

The structure of the blue zinc complex (**B**) was more difficult to deduce. The ^{1}H n.m.r. spectrum showed signals corresponding to sixteen pyrrole CH resonances and two NH resonances linked as 6 unprotonated pyrrole and 2 N-protonated pyrrole units as shown by decoupling and a COSY-45 spectrum, as well as overlapping multiplets due to eight phenyl groups.[10] In difference nuclear Overhauser experiments in which isolated pyrrole signals were saturated, another pyrrole proton was always found to be partly or completely saturated, thus showing that pairs of pyrrole protons are connected by chemical exchange, and hence that the blue material is a mixture of two interconverting species present in equal amounts. A two-dimensional chemical exchange n.m.r. spectrum (EXCSY) showed the complete mapping of one set of four pyrrole rings on to the other set of four pyrrole rings. The proton resonances on the pair of pyrrole rings bearing the benzoyl groups were identified by n.O.e. difference techniques (irradiating the deshielded *ortho* phenyl doublet at δ 8.01). This interconverting pair of pyrrole rings, like two other interconverting pairs, carried no protons; the remaining pair contained NH groups. The ^{13}C-n.m.r. spectrum of the blue zinc complex derived from *meso*-^{13}C-labelled TPP likewise showed four pairs of signals at 184.1 and 183.9, 145.4 and 144.4, 125.1 and 120.7, and 75.3 and 74.3 p.p.m. The two deshielded resonances are clearly due to benzoyl carbonyl groups, the middle two pairs to unsaturated (sp^{2}) *meso*-carbon atoms, and the most shielded pair to saturated (sp^{3}) *meso*-carbon atoms. The microanalysis[11] and mass spectrum of the crystalline blue complex were consistent with the molecular formula $C_{44}H_{30}N_4O_3Zn$, and the additional oxygen function was attributed to the presence of a hydroxyl group on a saturated *meso*-carbon atom as in the free base (**1a**). On the basis of these results, we propose that the blue zinc complex has the structure (**4**) with approximately tetrahedral coordination (presumably distorted towards planarity) around the zinc ion. This would exist in two diastereoisomeric forms which would be interconverted by inversion of configuration at the zinc atom, thus accounting for the n.m.r. results. Loss of water from this structure (**4**) would then give the observed conjugated yellow brown zinc complex (3,M=Zn). The NH groups have been drawn on pyrrole rings C; this is not certain and the protonation may be on rings A or B. However, it is certain that the protons remain on the same nitrogen atom in the two isomers.



(**4**)

A corresponding set of observations was made starting from the water adduct derived from ring-opened *meso*-tetra(4-methoxyphenyl)porphyrin. Again the blue product ($\lambda_{max.}$ 625 nm) showed a mixture of two isomers proved by two-dimensional n.m.r. spectroscopy.to be interconverting as before. Unfortunately, no additional conformational information could be obtained.

Fuhrhop and his coworkers isolated a yellow zinc complex from an analogous formylbilinone derived from octaethylporphyrin.[8] The crystal structure showed some distortion of the conjugated ligand from planarity presumably to relieve steric interactions, and addition of water as a fifth ligand. In the present case the steric repulsions in the yellow complex are more significant because of the large size of substituent groups and it appears that the complex tends to add water at a *meso* position to obtain greater relief.

Acknowledgements We thank INIC - Centro de Quimica de Meio Aquatico (Portugal) for support of this work, and the British Council for travel grants.

References and notes

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9 ^{1}H N.m.r. (360 MHz, $CDCl_3$): δ 5.61 (d, 1H, J=5.6Hz) coupled to 6.67 (d, 1H, J=5.6Hz), 6.57 (d, 1H, J=5.7Hz) coupled to 6.80 (d, 1H, J=5.7Hz), 6.60 (d, 1H, J=5.7Hz) coupled to 6.90 (d, 1H, J=5.7Hz, adjacent to Ph.CO), 6.92 (d, 1H, J=4.3Hz) coupled to 7.07 (d, 1H, J=4.3Hz), 7.47 - 7.7 (complex, 18H), 7.9 (d,2H, J=8Hz).

10 ^{1}H N.m.r. (360 MHz, $CDCl_3$): δ 5.11 (d, 1H, J=5Hz) coupled to 6.62 (d, 1H, J=5Hz), interchanging with 6.26 (d, 1H, J=5Hz) coupled to 6.65 (d, 1H, J=5Hz); 5.83 (dd, 1H, J=4,3Hz) coupled to 6.35 (dd, 1H, J=4,3Hz) and to 12.87 (NH, br), interchanging with 6.09 (overlapping) coupled to 6.45 (dd, 1H, J=4,3Hz) and to 11.12 (NH, br); 6.01 (d, 1H, J=4Hz) coupled to 6.47 (d, 1H, J=4Hz),interchanging with 6.10 (overlapping) coupled to 6.50 (d, 1H, J=4Hz); 6.11 (overlapping, adjacent to Ph.CO) coupled to 6.61 (d, 1H, J=5Hz), interchanging with 6.23 (d, 1H, J=4Hz, adjacent to Ph.CO) coupled to 6.52 (d, 1H, J=4Hz); 7.1-7.5 (complex, 18H), 8.01 (d, 2H, J=8Hz).

11 Found: C, 72.4; H, 4.2; N,7.6; ZnO, 10.8. Calc. for $C_{44}H_{30}N_4O_3Zn$: C, 72.6; N, 4.15; N, 7.7; ZnO, 11.2%).

(Received in UK 22 July 1992)