Importance of Macrocyclic Ring Deformation in the Facile Aerial Oxidation of Phenolic Porphyrins

Andrew J. Golder,[a] Lionel R. Milgrom,*[b] Kevin B. Nolan,*[a] and David C. Povey[a]

[a] *Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.*
[b] *School of Inorganic and Physical Chemistry, Kingston Polytechnic, Penrhyn Road, Kingston-upon-Thames KT1 2EE, U.K.*

Unlike its metal-free precursor and Ni[II] analogue, *meso*-tetrakis(3,5-di-t-butyl-4-hydroxyphenyl)-porphyrinatopalladium(II) undergoes very little aerial oxidation in basified dichloromethane, owing to metal-enforced planarity of the porphyrin macrocycle, as shown by crystal structure determinations of the two complexes.

One of the principal biological functions of tetrapyrrolic macrocycles is to mediate electron-transfer reactions in living cells. Thus, rapid oxidation and reduction of chlorophyll reaction centres drives the photosynthetic light reaction,[1a] while reversible oxidation of iron protoporphyrin IX determines the functioning of haemoprotein redox enzymes.[1b] This ability to mediate electron transfer[2a] also makes tetrapyrrolic macrocycles of interest as novel O_2-reduction catalysts,[2b] and organic conductors and semiconductors.[2c]

We recently reported a new type of porphyrin oxidation,[3a]

which has been used to model the action of the haem prosthetic group in cytochrome P450,[3b] and shows promise in O_2-reduction systems.[3c] Thus free-base porphyrin (**1**) undergoes facile two-electron aerial oxidation in basified CH_2Cl_2, to afford the porphodimethane-like compound (**2**). Cyclic voltammetry of (**1**)[3c] shows that its redox potential is significantly lowered in basified, as opposed to neutral, CH_2Cl_2, presumably by electron transfer from the phenolate substituents onto the macrocycle. This would involve some overlap between the π-systems of the substituents and the macrocycle, which means that deformations of the macrocycle must occur[4] so that the two π-systems can achieve a degree of coplanarity.

Metal complexation drastically affects the lability of (**1**) to air in basified CH_2Cl_2.[3c] Thus, $V^{IV}=O$, Mn[III], Sn[IV], and Pd[II] complexes of (**1**) are hardly oxidised, whereas Fe[III], Co[II], Ni[II], and Zn[II] complexes are fully oxidised.[3a,c] This is indicated by the visible spectral response of the basified-CH_2Cl_2 metalloporphyrin solutions to neutralisation with CF_3CO_2H.[3c] Thus, the Pd[II] complex, for example, shows virtually complete reappearance of the metalloporphyrin B band, whereas the Ni[II] complex does not. In this communication, we present evidence, based on the crystal structures of the Pd[II] and Ni[II] complexes of (**1**), which shows that the difference in chemical behaviour between the two complexes may depend on the
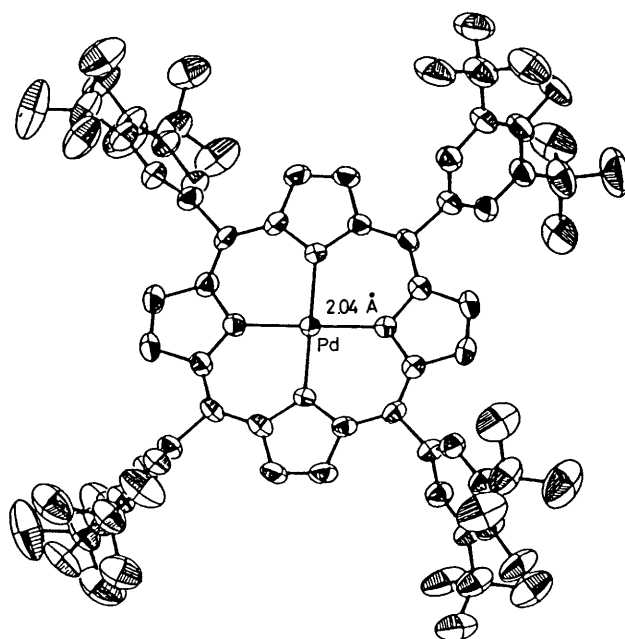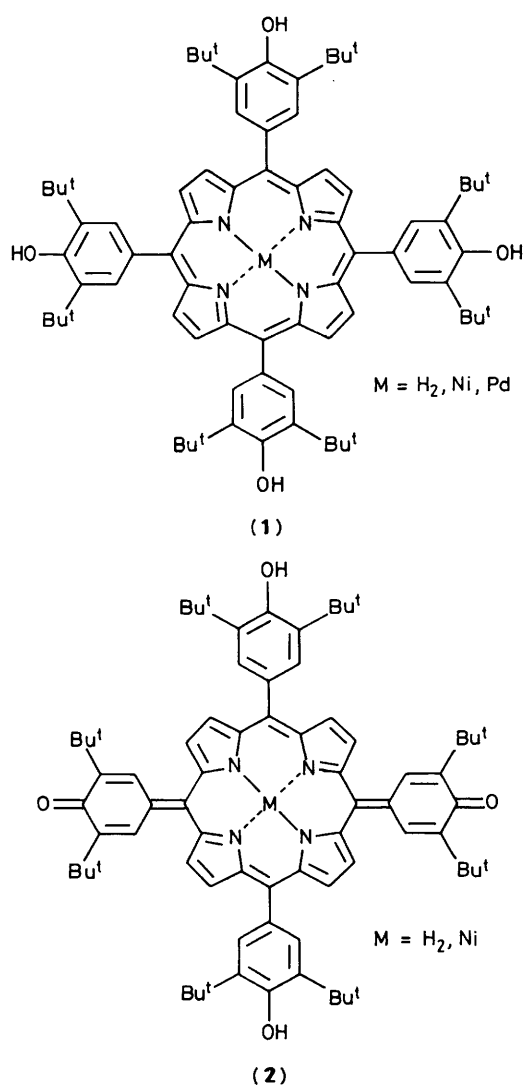

(**1**)

M = H$_2$, Ni, Pd

(**2**)

M = H$_2$, Ni

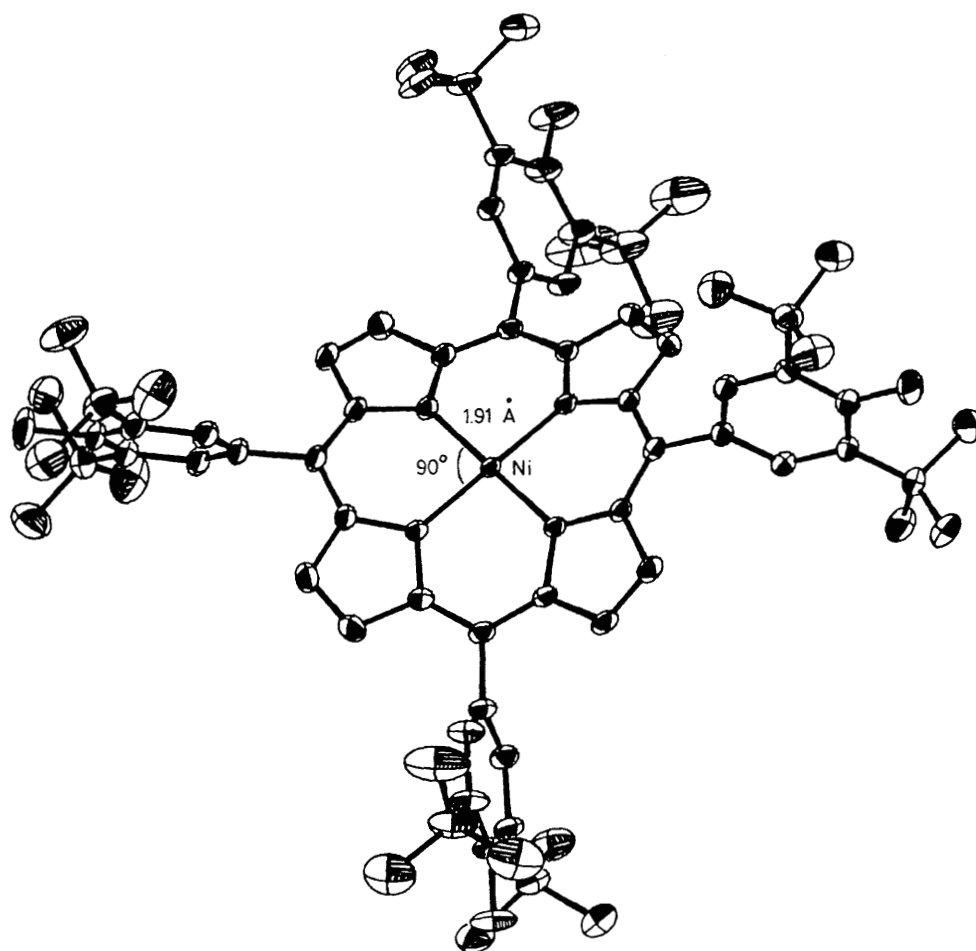**Figure 1.** ORTEP diagram of palladium complex of (**1**).

Figure 2. ORTEP diagram of nickel complex of (**1**).

ability of the phenolate π-system to interact with that of the porphyrin.

Molecular models indicate that such an interaction is impeded if the porphyrin skeleton is planar, but not if it is ruffled. The crystal structure of the Pd^{II} complex of (**1**) shows that the macrocycle is planar† (Figure 1). This allows little

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† *Crystal data*: $C_{76}H_{92}N_4O_4Pd\cdot3C_6H_{12}$, mononclinic, space group $C2/c$, $a = 28.004(4)$, $b = 26.871(7)$, $c = 21.267(2)$ Å, $\beta = 131.18(2)$, $U = 12045.4$ Å^3, $Z = 4$, $D_c = 0.189$ g cm^{-3}; $R = 0.083$. All atoms in the metalloporphyrin skeleton are coplanar, with Pd–N bond distances 2.022(1) Å. The porphyrin molecules are hydrogen bonded [O–H · · · O; O–O separation 2.85(1) Å] together in sheets with cyclohexane (solvent) molecules between the sheets. The dihedral angle between the phenyl rings and the porphyrin plane is ±67.6°.

$C_{76}H_{92}N_4O_4Ni$: triclinic, space group $P\bar{1}$, $a = 14.820(2)$, $b = 15.398(2)$, $c = 18.822(1)$ Å, $\alpha = 75.35(6)$, $\beta = 69.74(3)$, $\gamma = 87.31(3)°$, $U = 3894.5$ Å^3, $Z = 2$, $D_c = 1.01$ g cm^{-3}; $R = 0.068$. The molecule contains a square-planar Ni–N$_4$ unit, Ni–N = 1.91 Å; the porphyrin core is ruffled with the *meso*-carbon atoms alternatively displaced ±0.55 Å from the mean atom plane, resulting in angles of 23.4—35.1° between adjacent pyrrole rings. The dihedral angle between the phenyl rings and the mean porphyrin plane lie between ±63.3 and ±83.4°.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.
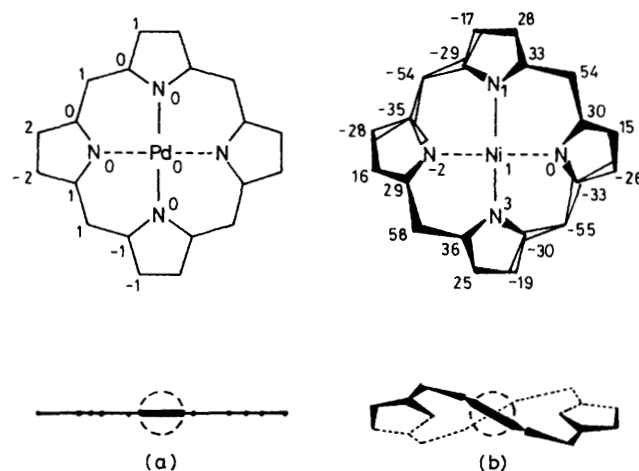

Figure 3. Deviations from mean porphyrin plane for (a) palladium and (b) nickel complexes of (**1**) in units of 0.01 Å. Negative quantities are below the mean plane, positive above.

change in the phenolate–porphyrin dihedral angle, such that the two π-systems are virtually isolated from each other. Consequently, no appreciable aerial oxidation of the Pd^{II}

complex is expected in basified CH_2Cl_2, as is observed.[3c] The Ni^{II} complex, on the other hand, contains a highly ruffled porphyrin macrocycle† (Figure 2). This allows a greater degree of rotational freedom between the porphyrin and the phenolate substituents[4] for the Ni^{II} complex compared with the Pd^{II} analogue. Consequently, there will be more opportunity for overlap between the phenolate and macrocyclic π-systems, so that aerial oxidation of the Ni^{II} complex in basified CH_2Cl_2 is expected and observed.[3c]

The structural differences between the Ni^{II} and Pd^{II} complexes are largely due to the different ionic radii of the metal atom.[5] A planar metalloporphyrin has an ideal central 'hole' of about 2.01 Å,[6] so that the metal–ligand bond distances in the Pd^{II} complex [2.022(1) Å] are compatible with porphyrin planarity. The unusual, sheet-forming system of intermolecular hydrogen bonds, exhibited by the Pd^{II} complex† might also contribute to the imposition of planarity on the macrocycle.

In order to co-ordinate to the much smaller Ni^{II} cation, and form Ni–N bonds, the porphyrin macrocycle is forced to undergo a radial contraction that gives rise to severe ruffling of the macrocycle,[5] compared to the Pd^{II} complex (Figure 3). The resultant tilting of adjacent pyrrole rings allows the variation in dihedral angle between the phenyl rings and the mean porphyrin lane, that we believe leads to aerial oxidation of the Ni^{II} complex in basified CH_2Cl_2.

In conclusion, we have indicated that the metal-cation-controlled deformation of the porphyrin macrocycle (1) will be an important factor determining the facility of its aerial oxidation. If so, then the choice of metal is crucial for the practical application of these complexes as, for example,

electroactive coatings with which to modify electrodes, and as oxygen-reduction catalysts in fuel cells.

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