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REDUCTIVE DEMETALLATION OF PORPHYRINS: EVIDENCE FOR PERIPHERAL AND AXIAL MODES OF REDUCTION

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ABSTRACT: Experiments with isotopically-labelled and sterically-constrained porphyrins have been used to elucidate demetallation pathways for silver and copper porphyrins.

It has been appreciated for some time that porphyrins can undergo redox reactions via axial or peripheral pathways[1] but there has been little definitive evidence for mechanisms in individual cases. Collman et al[2] have reported the use of $NaBH_4$ as a demetallation reagent for silver porphyrins, while we have found that in the case of copper porphyrins, a $Cu^{2+}/NaBH_4$ mixture reductively removes the metal; borohydride alone does not remove Cu^{2+}. We have probed this difference at a mechanistic level using deuterium isotope experiments and sterically-constrained porphyrins.

The reductive removal of silver or copper from porphyrins involves electron addition either by (a) electron tunnelling [Fig. 1) or (b) addition followed by elimination [Fig. 2]. Use of $NaBD_4$ followed by mass spectrometric analysis afforded a means of differentiating (a) and (b) for the silver (II) and copper (II) derivatives of octaethyl porphyrin (OEP; 1) and with the same compounds deuterated at the meso positions.[3] The results are summarised in Table 1.

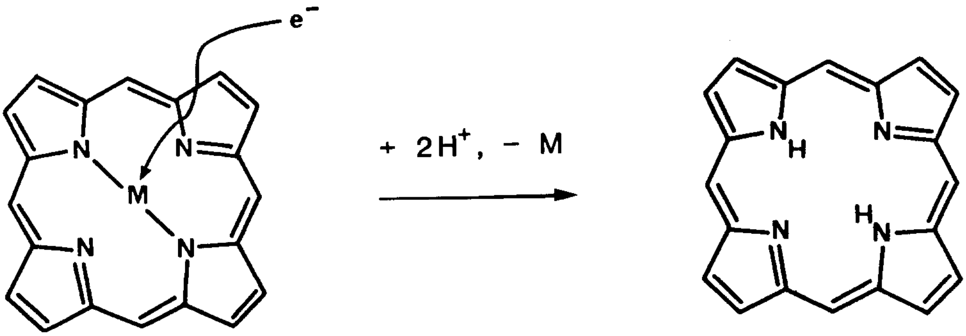


Figure 1: Reduction via electron tunnelling.

TABLE 1 Deuterium Incorporation in Reductive Metallations

EXPT	PORPHYRIN	SOLVENT[a]	REAGENT	AVERAGE NO. DEUTERIUMS INCORPORATED PER MOLE
(1)	AgOEP	MeOD	BH_4^-	0.125
(2)	AgOEP	MeOH	BD_4^-	0.43
(3)	OEP	MeOD	BD_4^-	0.04
(4)	AgOEP	MeOD	BD_4^-	1.40
(5)	AgOEP-d_4	MeOH	BH_4^-	0.33[b]
(6)	AgOEP	$(CH_3OCH_2CH_2)_2O$	BD_4^-	0.05

a THF as cosolvent (ratio 1:1); b Number of protons incorporated.

In those cases showing a significant incorporation of deuterium, an approximately normal distribution was obtained over the series OEP-d_0 to OEP-d_4, multiple deuterium incorporation suggesting that the reaction is reversible. Meso substitution was verified by NMR spectroscopy.

A 1:1 mixture of BH_4^-/BD_4^- in MeOH gave virtually no deuterium incorporation, implying that boron-hydrogen/deuterium bond cleavage is important. Control experiments using BD_4^-in MeOH to reduce an aldehyde gave significant amounts of hydride addition product, hence the lower deuterium incorporation in Expt. 2 [Table 1] can be rationalised by this solvent exchange coupled with the isotope effect noted above. In Expt. 1, exchange with MeOD again leads to deuterium incorporation. Comparison of Expts. 4 and 5 suggests an isotope effect in the proton leaving step of the addition-elimination mechanism, resulting in lower incorporation of hydrogen into the deuterated ligand.

The absence of deuterium incorporation into a high proportion of OEP molecules in Expt 4 suggested an alternative route by electron tunnelling, which is defined here to be direct electron addition to the metal or through the π-system. Borohydride attack, which depends on S_N2 type displacement by a nucleophilic solvent, can be made slower by the use of less nucleophilic solvents.[4] In diglyme no deuterium was incorporated (Expt. 6) since the addition/ elimination route became very much slower than electron tunnelling.

Based on this evidence, we suggest that, in the case of silver porphyrins, borohydride reductive demetallation can occur both by electron tunnelling and by the route shown in Figure 2. A mechanism involving peripheral attack is supported by the ease of reductive demetallation that we observe in the capped porphyrin (2) and the porphyrin dimer (4).

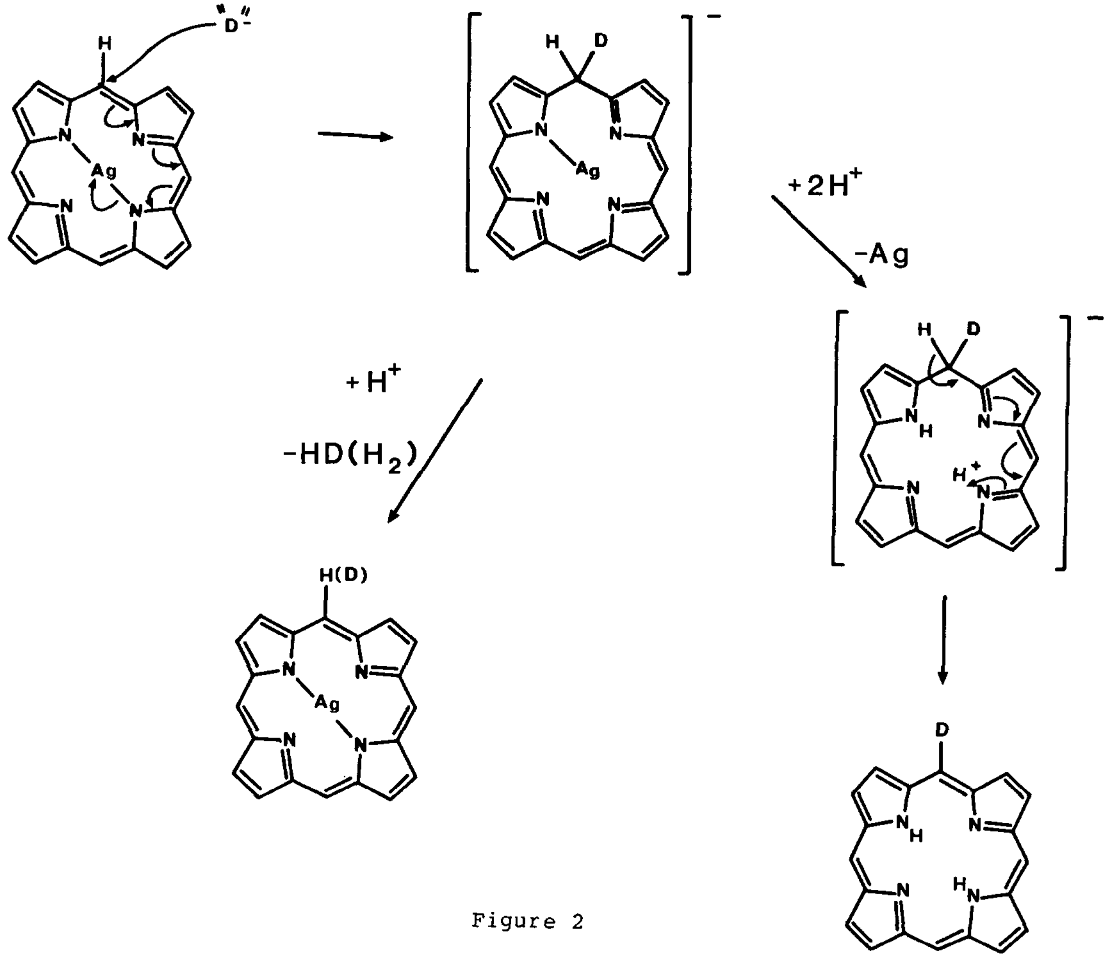
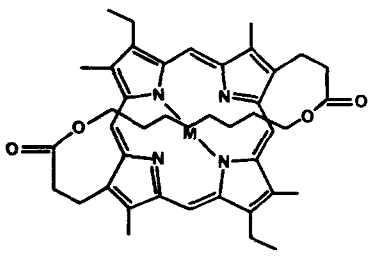
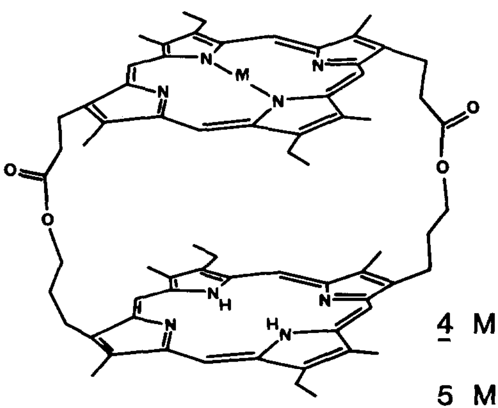


Figure 2



2 M = Ag

3 M = Cu



4 M = Ag

5 M = Cu

In marked contrast, no deuterium is incorporated when CuOEP is reduced by $Cu^{2+}/NaBH_4$, and Cu^{2+} is not removed at all from the porphyrin cofacial dimer (5). The absence or presence of Mg or Zn in the lower porphyrin moiety of (5) has no effect. It appears, therefore, that reductive demetallation of Cu-porphyrins with this reagent requires attack of the reducing agent on one face of the porphyrin, the central metal ion then leaving from the opposite side of the molecule. NMR studies on dimers indicate that the porphyrin planes are closely packed with an offset geometry accounting for the steric barrier to loss of copper.[5] This notion is supported by the observation that the capped porphyrin (3) is demetallated, but only very slowly. It is known that the alkyl cap is flexible,[6] and it is therefore reasonable to expect that it can be deformed sufficiently to allow either the attacking reagent, or the departing Cu^{2+} ion, to 'squeeze' by. The axial attack of reducing agent on the porphyrin face maybe directly on the metal, or *via* the π-system.

Experimentally, these reductions are straightforward. To a solution of the Ag porphyrin in THF/MeOH (1:1) is added an excess of $NaBH_4$ with stirring. After a minute or two, the solution becomes discoloured, dichloromethane is added, and the porphyrin is isolated by chromatography over alumina. The same procedure is used for copper porphyrins except that the THF/MeOH solution is first saturated with $Cu(OAC)_2$.

The results presented here not only throw new light on the mechanisms involved in these particular reactions, but also demonstrate the potential of sterically-constrained porphyrins in delineating mechanisms.

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