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A General Synthesis of Mixed Metal Porphyrin Cofacial Dimers

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The use of zinc as a protecting group offers a short general route to a wide range of mixed metal porphyrin cofacial dimers.

Bismetallo(porphyrin) complexes have become increasingly important in the investigation of various photochemical and redox processes. Such systems have been developed to mimic multielectron redox enzymes such as cytochrome oxidase, and more especially those of, as yet, indeterminate structure.¹⁻³ Other types of complex, in particular those containing porphyrin ligands, can help to illustrate the importance of distance, energy, and structure in the control of electron transfer in photosynthesis and in the design of molecular systems for photochemical energy storage.⁴ In addition, however, mixed metal systems are of inherent interest with regard to the study of metal-metal interactions in complexes of predetermined geometry.

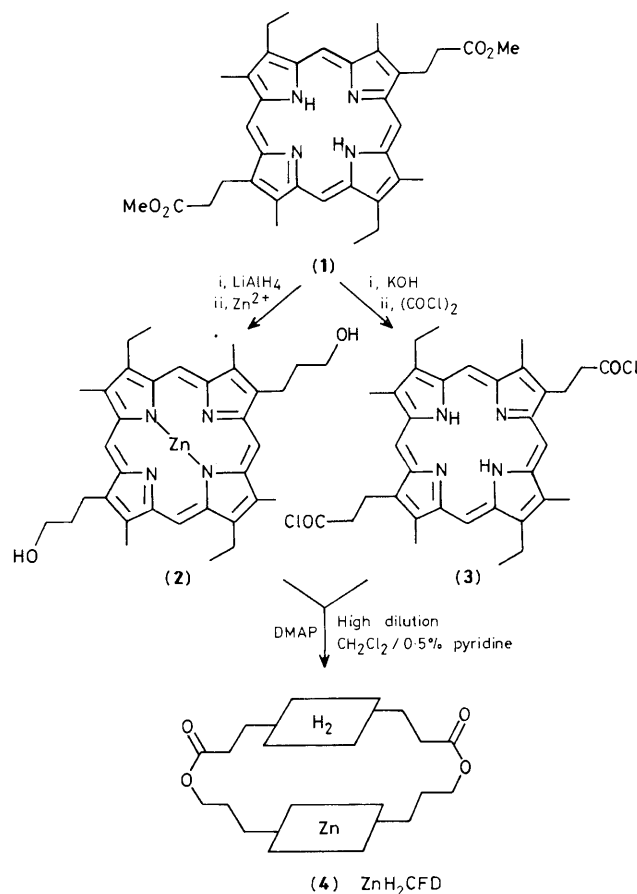
In connection with our own interests in the electron transfer chemistry of porphyrins⁵ we have synthesised a series of porphyrin cofacial dimers (CFD) containing a range of metal ions. In particular we wanted to be able to control separately the nature and oxidation states of the metal ion in both faces of the dimer. One approach would be to couple two porphyrins which are premetallated. This is possible but unsatisfactory as it requires a separate, and usually low yielding, coupling for each new compound.^{2,3,6} A more attractive approach is to synthesise a porphyrin dimer containing a removable metal as a protecting group for one porphyrin face. Collman *et al.*² have described such a route, using silver as the protecting group and borohydride reduction as the deprotection step. The latter is unfortunately incompatible with the presence of reducible metals such as Co^{III}, Fe^{III}, and Mn^{III}. We show here that the use of Zn, which is readily removed by dilute acid, allows the synthesis of a virtually unlimited range of mixed metal porphyrin dimers, conveniently and in high yield.

The porphyrin acid chloride (3) and zinc porphyrin diol (2) were each prepared from the ester (1) in high yield (Scheme 1). Compounds (3) and (2) were coupled at room temperature under high dilution in CH₂Cl₂ containing 4-*N,N*-dimethylaminopyridine (DMAP) and 0.5% pyridine to give ZnH₂CFD (4) in 40% yield. The pyridine is crucial. Intermolecular zinc to hydroxy bonding in (2) renders the compound virtually insoluble in non basic solvents; pyridine competes effectively for the zinc in (2), thereby disaggregating and solubilising the compound.

A variety of metals can then be inserted into the free base moiety of ZnH₂CFD (4) to give the mixed metal dimers,

ZnMCFD. Examples (Table 1) include Co^{III}, Mn^{III}, and Fe^{III} (as halide salts); relatively normal insertion procedures *via* divalent metal salts are used,^{6,7} except that very acidic conditions are avoided.

In the course of our metallation studies we observed that FeCl₃ rapidly demetallates zinc porphyrins. Since FeCl₃ does



Scheme 1

Table 1. Mixed metal porphyrin cofacial dimers (MM'CFD) synthesised using zinc as a protecting group.^a

Neutral species		Salts		
M	M'	M	M'	X
Zn	H ₂	Zn	Co ^{III}	Br, Cl
Zn	Ag	Zn	Mn ^{III}	Br, Cl
Zn	Cu	Zn	Fe ^{III}	Cl
Zn	Co ^{II}	H ₂	Co ^{III}	Br, Cl
Ag	Cu	H ₂	Mn ^{III}	Br, Cl
Co ^{II}	Cu	H ₂	Fe ^{III}	Cl
		Co ^{II}	Fe ^{III}	Cl
		Co ^{II}	Co ^{III}	Br, Cl
		Co ^{II}	Mn ^{III}	Br
		Co ^{III}	Mn ^{III}	Br

^a H₄CFD, the free-base parent compound, was characterised by microanalysis, u.v., n.m.r., and mass spectroscopy. Metallated derivatives were characterised by n.m.r., u.v., and mass spectroscopy or electrochemical methods, as appropriate.

not metallate porphyrins, demetallation cannot be due to a transmetallation process. It is probable that zinc is removed by the acidity of FeCl₃; demetallation due to a radical mechanism by the oxidising action of FeCl₃ being less likely, although we have observed demetallation of zinc porphyrins during bromine oxidation.

In general, zinc can be removed from ZnMCFD or ZnMCFD+X⁻ by treatment with dilute acid (16% aqueous HBr), and the resulting H₂MCFD remetallated to give a wide range of MM'CFD. Overall yields from ZnH₂CFD are

77–86%. Table 1 lists compounds which have been made by this route to date. This by no means represents an exhaustive collection and there are many other possibilities. Clearly this approach would be applicable to porphyrin dimers of other geometries.

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