Axial Ligation Equilibria as Probes of the Effective Steric Bulk of Substituted Metallo-Tetraarylporphyrin Complexes

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The strategy of placing large substituents at the ortho and meta positions of tetraarylporphyrin compounds has long been used to sterically encumber the face of a porphyrin and thereby suppress unwanted reactions. A similar approach is used in the synthesis of dendrimeric porphyrin compounds.

Recently, we used octasubstituted tetraarylporphyrins to establish that the alkyl exchange reaction of alkyl-cobalt(III) porphyrin complexes with cobalt(II) porphyrin complexes proceeds via a bimolecular, S_H2 mechanism. However, our results suggested that the relationship between the effective steric bulk of substituents and their size and position may not be straightforward. We report here the results of an investigation of that relationship.

Equilibria constants and thermodynamic parameters for coordination of a range of axial ligands to a series of zinc(II) complexes of substituted tetraarylporphyrins were determined. The zinc complexes were investigated because they have simple 1:1 equilibria that are readily investigated by UV/vis spectroscopy, are generally redox innocent under the conditions of the ligation reactions, and have a sufficiently large K_{eq} in unhindered cases that K_{eq} for hindered cases might still be determined accurately. The axial ligands used included substituted pyridines, phosphines, phosphates, and proazacyclophosphatranes. The porphyrin compounds included TTP, *meso*-tetra-*p*-tolylporphyrin; T2,6MeOPP, tetrakis(2,6-dimethoxyphenyl)porphyrin; T2,6FBzOPP, tetrakis(2,6-bis(perfluorobenzyloxy)phenyl)porphyrin; and TBPMPP, tetrakis(3,5-bis(*o*-biphenylmethoxy)phenyl)porphyrin.

Experimental results suggest that in a functional sense, TBPMPP is not hindered at the metal center relative to TTP. In contrast, both ortho substituted porphyrins have significant hinderance. Cone-shaped ligands are generally unable to coordinate to either T2,6MeOPP or T2,6FBzOPP complexes. Interestingly, for coordination of planar ligands, the methoxy groups of T2,6MeOPP present a greater effective steric bulk than the perfluorobenzyloxy groups of T2,6FBzOPP. This appears to be an entropic effect.

The small effective steric bulk of the meta-biphenylmethoxy substituents was confirmed by the successful synthesis of the μ-oxo bridged complex, $[Fe(TBPMPP)]_2O$. This complex, which is antiferromagnetically coupled, was identified by the characteristic chemical shift of its pyrrole protons. Thus, it would appear that the 8 biphenylmethoxy groups on the two porphyrin faces adjacent to the μ-oxo bridge spend little time in the region between the two porphyrins.