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Axial Ligation of Oxygen Donors to Tetraphenylporphyrinatocadmium (II) *

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Both important classes of natural metalloporphyrins, the iron porphyrins and magnesium chlorins, have their function associated with axial ligation phenomena. Therefore, a detailed study of axial coordination in metalloporphyrin seems necessary.

Axial ligation of a variety of oxygen donors to meso-tetraphenylporphyrinatocadmium(II) [Cd(TPP)] was studied in dichloromethane by the spectroscopic method. Addition of oxygen donors to Cd(TPP) caused red shifts in the absorption spectrum. The magnitude of the red shift was dependent on the charge of the axial ligands. A weak relationship between the ratio of molar extinction coefficients of alpha bands to that of beta bands and the wavenumber of the Soret band was observed.

Dissociation constants were determined for Cd(TPP)-ligand complexes. A 1 : 1 bindng stoichiometry is found in all cases. Increasing affinity for complex formation as a function of increasing basicity is observed among a limited set of structurally similar ligands. Steric constraints also strongly influence ligand binding affinity.

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