

Photooxidation of nickel(II) macrocyclic complexes from the charge-transfer-to-solvent excited states

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Nickel(II) macrocyclic systems with saturated and unsaturated tetraaza type ligands show intense absorption bands in the ultraviolet region and the excited states exhibit the characteristics of charge-transfer-to-solvent transitions. Investigations of the photochemical pathways in acetonitrile, dichloromethane, and water using flash kinetic spectroscopic techniques reveal different reaction products. The primary photochemical reaction involves oxidation of the metal centre leaving the ligand unaffected in most cases. The role of the solvent and dissolved oxygen primarily determine the nature of the products. Flash photolysis investigations have shown details of the reactions of the oxidised nickel(III) complex with the transient species present in the solution. Photoproducted nickel(III) macrocyclic complexes have been isolated in a few cases and the structures elucidated. Structural information and results of the flash photolysis studies are presented.