

Coordination aggregation of mesoaryl substituted porphyrins

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Abstract. Synthesis of the free-base *tetrakis* (3'-nitro/aminophenyl), (H_2 TNP/ H_2 TAP) has been accomplished and its coordination behaviour towards Mg(II), Co(II), Zn(II) and Ag(II) ions is investigated. Optical and magnetic resonance properties of the metal derivatives MTNP and MTAP reveal that the aminoporphyrins exist as aggregates in solution. The aggregation is promoted by the coordination of the peripheral amino groups to neighbouring metalloporphyrins. Possible structures of aggregated species are proposed from the model studies.

Keywords. Metalloporphyrins; axial coordination; coordinated aggregates.

1. Introduction

The extensive occurrence of aggregated porphyrinoid molecules in biological systems has spurred a great deal of research activity. The design and syntheses of biomimetic models involving more than one porphyrin unit has attracted wide attention. The strategy adopted to obtain these systems lies in the proper choice of substituents and metal ions that promote dimerisation/oligomerization of porphyrins in solution. The presence of potentially ligating substituents such as sulphanato, carboxylato and dimethyl amino groups at the aryl positions of 5,12,15,20-tetraphenylporphyrins (TPP) enhances the association property of the porphyrins (Pasternack *et al* 1973; Ojadi *et al* 1985; Koehorst *et al* 1988). The metalloporphyrins involving divalent metal ions that exhibit the least tendency to associate with solvent molecules predominantly exist as oligomers in solution. On the other hand, the metal (II) ions that easily form 5 or 6 coordinated species with solvent molecules are essentially monomeric in nature. Abraham *et al* (1977, 1978) have shown that the extent of aggregation of metal derivatives of deuteroporphyrin IX dimethylester is related to the strength of the porphyrin-metal interaction in the case of zinc, cadmium and palladium porphyrins.

An interesting approach to achieve oligomerization of tetraphenylporphyrin in solution is to have ligating substituents (of the aryl group) at specific orientation with strongly coordinating metal ions in the porphyrin cavity. Model building studies have suggested that substitution of the donor groups at the meta positions of the phenyl groups of TPP favours formation of aggregates. Here, we report the studies on coordination behaviour of 5,10,15,20-tetra (3-aminophenyl) porphyrin (H_2 TAP) and the corresponding nitro derivative, (H_2 TNP), which is the precursor of H_2 TAP (figure 1). A comparison of the coordinating abilities of H_2 TAP and H_2 TNP towards the metal(II) ions (Co, Ni, Cu and Zn) clearly brings forth the importance of axial ligation in the aggregate formation.

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