

Complex formation of ferric protoporphyrin IX from the reaction of hemin with ammonia and small aliphatic amines

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Abstract

Complexes of Fe^{III} protoporphyrin IX (Fe^{III} PPIX) with the amido anion were obtained from the reaction of Fe^{III} PPIX chloride (hemin) with ammonia and small aliphatic amines under solvent free conditions. The reaction of hemin with gaseous ammonia leads to a pentacoordinated complex at the iron site, PPIX-Fe-NH_2 , plus NH_4Cl , while at the peripheral propionic acidic groups ammonium carboxylate is formed. The corresponding stoichiometry (1:4 molar ratio of hemin to ammonia) was confirmed by the adsorption isotherm. Analogous reactions and complex formation were observed with EtNH_2 and Et_2NH . These reactions were monitored using X-ray diffraction (XRD), and i.r. and Mössbauer spectroscopies. The isomer shift and quadrupole splitting values of the resulting complexes are in correspondence with the strong σ -donor character of the amido anion linked to the iron atom. For comparison, the Mössbauer parameters for hemin complexes with arginine and 2-aminoguanidine, which also have pure σ interaction with the porphyrin iron, were included and discussed.

Introduction

The complexes of iron protoporphyrin IX (FePPIX) with nitrogenous bases have been extensively studied [1–5], mainly in connection with the role of the FePPIX moiety in important biomolecules, *e.g.* haemoglobin, myoglobin and cytochromes. It seems that the functional properties of these biomolecules are closely related to the coordination chemistry of the iron atom, particularly by steric and electronic effects due to its axial ligands. In the majority of cytochrome proteins the iron atom is coordinated to two histidine molecules at their imidazole residue [5, 6]. Many of the observed properties in these proteins have been ascribed to the role of the orientation of the two imidazole planes of the iron bonded histidines and to their bond properties effect on the iron atom reactivity [2–5]. Since these ligands are involved in σ - and π -interactions with the porphyrin iron, much of the reported work on FePPIX complexes has been oriented to shed light on the probable role of these interactions in the functional properties of these biomolecules. In this sense extensive studies of FePPIX complexes with *N*-heterocycles (*e.g.* imidazole and its derivatives) and with aliphatic amines

have been reported [1–10]. While in aliphatic amines only the σ mechanism can be present, *N*-heterocyclic can also participate in a π -interaction with the porphyrin iron. These complexes are usually obtained from solutions but with small aliphatic amines (ammonia, methyl-, ethyl-, dimethyl-, diethyl- and triethyl-amine) the preparation of Fe^{III} PPIX complexes fails, which has been tentatively attributed to a dominant amine–water interaction [4]. It has been reported that complexes of *N*-heterocycles with Fe^{III} PPIX are weaker than those with Fe^{II} PPIX [4]. It is also known that complexes of Fe^{II} PPIX with aliphatic amines are much weaker than those with *N*-heterocycles ligands [4]. From these facts it can be inferred that the Fe^{III} PPIX complexes with aliphatic amines are the weakest and their formation could be hindered by interactions with the solvent.

In previous papers we have reported the preparation of Fe^{III} PPIX complexes in the absence of solvent [11–13]. In some cases the interaction with a solvent can destroy complexes previously formed in the solid state [11]. This suggests the possibility of Fe^{III} PPIX–amine complex formation in the absence of solvent, particularly for small aliphatic amines. In this contribution we report the formation of Fe^{III} PPIX complexes with the amido anion (R_2N^-) which is formed in the reaction of hemin with ammonia, ethylamine and diethylamine. The reaction products were characterized

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