# Phenanthroline-assisted Metallation of a Porphyrin: Copper and Silver Mixed Valence Homodinuclear Complexes

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The complexation of copper(II/I) and silver(II/I) in a phenanthroline capped porphyrin ligand has been studied and shows the formation of mixed valence homodinuclear complexes together with a kinetically enhanced complexation within the porphyrin core.

There is a growing interest in ligands able to provide coordination sites for transition metals within controlled geometry and topography,[1-5] thus enabling the study of metal–metal interactions and cooperativity in order to obtain model compounds for important biological processes such as tetraelectronic reduction of oxygen by iron/copper systems in the cytochrome c oxidase.[6-9] We have recently described the synthesis of a phenanthroline capped porphyrin (porphen) 1[10] which combines in a rigid fashion a 2,9-diphenyl 1,10-phenanthroline (phen) unit and a *meso*-diphenyl porphyrin at a distance of *ca* 6.5 Å. Owing to the nature of both binding subunits, coordination of square planar or octahedral transition metals in the porphyrin core as well as a restricted coordination to tetrahedral transition metals in the phenanthroline was expected. We report herein the preliminary binding studies on copper and silver ions which exhibit interesting kinetic and electrochemical properties.
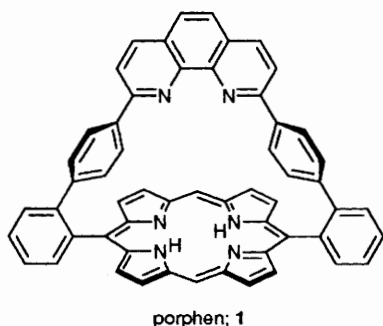
Complexation of copper(I) and silver(I) was studied in N,N-dimethylformamide (DMF) using $Cu^I(MeCN)_4PF_6$ and Ag^INO_3 and followed by either UV–VIS spectroscopy or cyclic voltammetry (CV) [Pt electrodes, CH_2Cl_2–0.1 mol dm^{-3} tetrabutylammonium perchlorate (TBAP)]. Comparison with precursors and similar compounds was possible studying 5,10,15,20-tetraphenylporphyrin (H_2tpp) and 2,9-ditolyl 1,10-phenanthroline in the same experimental procedures.

For a metal : ligand ratio of 1 : 1, instantaneous complexation occurring in the phen unit was detected by the spectral changes in the UV region for silver(I) and copper(I) while for
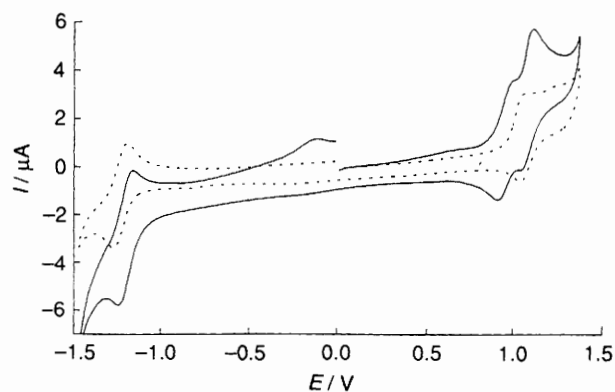
porphen; 1

Fig. 1 Cyclic voltammograms of porphen (- - - -) and porphen + 1 equiv. $Cu(MeCN)_4BF_4$ (———) in CH_2Cl_2 + 0.1 mol dm^{-3} TBAP, Pt electrode, sweep rate 0.1 V s^{-1}
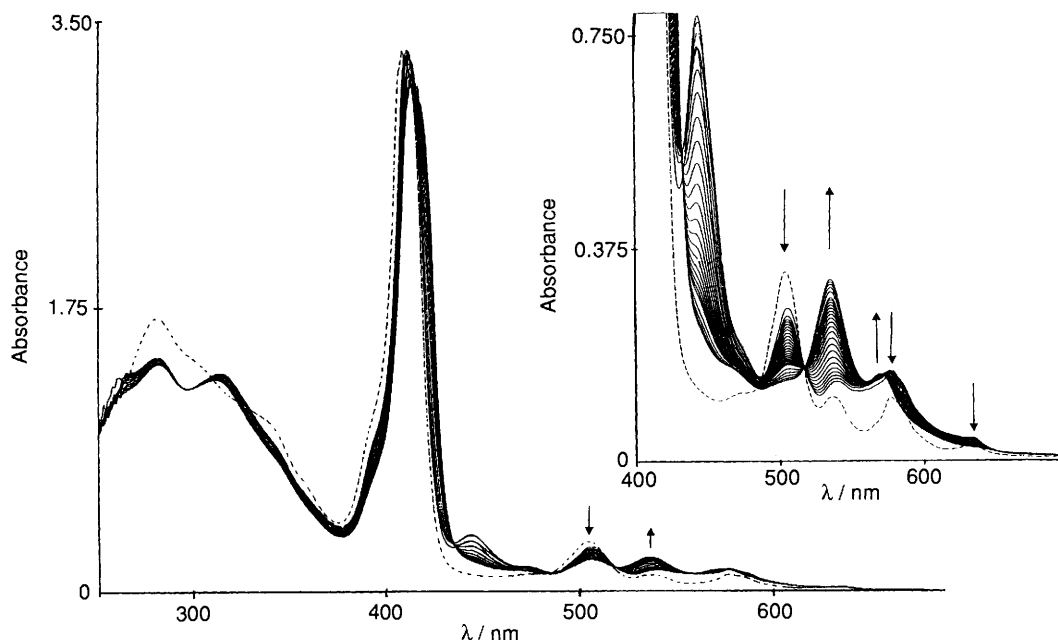
Fig. 2 Time dependence of the porphen UV–VIS absorption spectrum in DMF [porphen] = 2.5 × 10⁻⁵ mol dm⁻³ in presence of Agᴵ, metal : ligand (M : L) ratio = 35; (- - -): free base; (————): spectra after addition of Agᴵ recorded every 3 min. Inset: expanded visible part of the spectra.
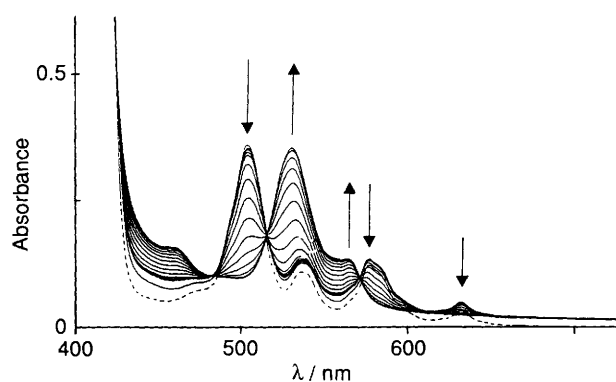

Fig. 3 Time dependence of the porphen VIS absorption spectrum in DMF [porphen] = 2.5 × 10⁻⁵ mol dm⁻³ in the presence of Cuᴵ, M : L ratio = 7; (- - -): initial spectrum; (————): spectra recorded every 3 min after addition of Cuᴵ

Fig. 4 Kinetic complexation of porphen (●) and H₂tpp (○) in DMF, [c] = 2.5 × 10⁻⁵ mol dm⁻³, in presence of Cu(MeCN)₄BF₄, M : L ratio = 7

copper(ɪ), the rise of a new reversible charge transfer at +0.95 V vs. SCE (saturated calomel electrode) in the cyclovoltam-mogram (Fig. 1) confirms the formation of the phenanthrol-ine-Cuᴵ complex.

When the metals are present in an excess, the changes observed in the visible region of the spectra depicted in Figs. 2 and 3 are consistent with metallation of the porphyrin core. In both cases, the metals complexed in the porphyrin were respectively oxidized to silver(ɪɪ) and copper(ɪɪ). During this process, an intermediate Agᴵ-porphyrin complex was detected by the presence of its typical Soret band at 450 mm¹¹ which rapidly disappeared as the silver(ɪ) complex evolved towards silver(ɪɪ) (Fig. 2). Similar observations were obtained for H₂tpp as a model of the porphyrin site or porphen. For silver(ɪ) the UV region of the spectra is consistent with the complexation of Agᴵ in the phen site. In the case of copper, the typical bands of copper(ɪ)-phen complexes were hidden by the absorption of copper(ɪ) in large excess, but the dinuclear mixed-valence complex porphen-Cuᴵᴵ/Cuᴵ can be readily obtained by mixing 1 equiv. of the metalloporphyrin deriva-tive porphen-Cuᴵᴵ complex, quantitatively isolated from the
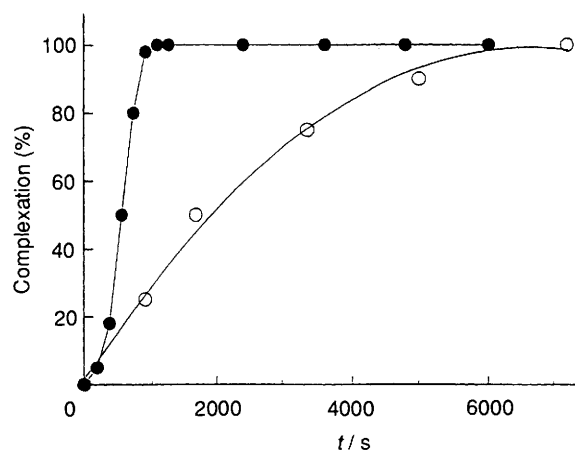
metallation of 1 with copper(ɪɪ) acetate, with 1 equiv. of Cuᴵ(MeCN)₄ in CH₂Cl₂.†

Concerning the rate of complexation within the porphyrin core, the presence of a phen site close to the porphyrin unit has a significant enhancing effect in both cases. For example, as shown in Fig. 4, the formation of the Cuᴵᴵ-porphen complex was complete after 1000 s compared to 6000 s for the tpp complex. For silver, the formation of the Agᴵᴵ-porphen complex was complete after 3000 s. The surprising complexing properties of porphen compared with those of H₂tpp cannot be explained by a deformation of the porphyrin nucleus induced by the phen unit as, from structural data,¹² neither distortion of the porphyrin subunit, nor distortion of the phen unit were observed. Obviously, the complexation of silver(ɪɪ) and copper(ɪɪ) in the porphyrin subunit of 1 is kinetically enhanced compared to H₂tpp. The phen site can play several roles in this process, for example in a predesolvation process

† Positive FAB mass spectral data: M⁺(100%) at m/z = 916.1 for C₅₆H₃₂N₆Cu₂ and M⁺ − Cu at 852.2.

or in lowering the oxidization potentials of silver(I) and copper(I) which need to be oxidized while entering the porphyrin core. Although the tendency is similar, the weaker enhancement of Ag^{II} complexation compared to Cu^{II} may be explained by the formation of an intermediate Ag^I-porphyrin complex during the metallation of the porphyrin core while no evidence for a Cu^I-porphyrin complex has ever been obtained during the metallation process. Therefore, when Cu^I and Ag^I are added to the ligand, competition between the porphyrin core and the phenanthroline site may occur for Ag^I but not for Cu^I.

In conclusion, in the presence of copper(I) and silver(I), the porphen ligand forms mixed-valence homodinuclear products in which the phen site complexes the monovalent form of the metal ion and the porphyrin core binds the divalent metallic cation. The rate of complexation of the metal within the porphyrin site is strongly enhanced by the proximity of the phen subunit. More detailed kinetic and mechanistic studies are under way in order to determine the exact influence of the phenanthroline on the complexation. Also, the above reported results lead to the reasonable expectation that such ditopic ligands will generate heterodinuclear complexes.

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