meso-α,α,α,α-Tetra(*o*-nicotinamidophenyl)porphyrin: a Novel Ligand for the Preparation of Unsymmetrical Bis-metal Complexes

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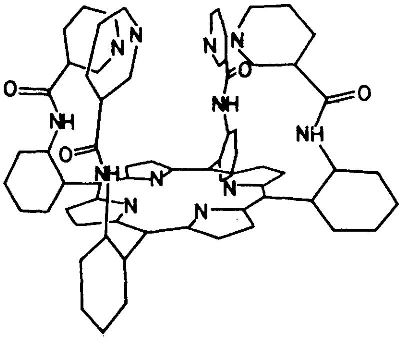
ummary The synthesis and brief characterization of the novel ligand (**1**) capable of accommodating two metal ions in dissimilar square-planar co-ordination sites is described; the ligand is based on a tetraphenylporphyrin having four pyridine molecules appended to it such that a second square-planar co-ordination site is formed above the porphyrin plane.

Several bis-metal complexes have been prepared which have potentially the correct geometry to co-ordinate small molecules like dioxygen simultaneously between two metal atoms.[1,2] These compounds are important because they are potentially multielectron redox catalysts and may also serve as enzyme models.

Some of the more interesting ligands in this class are composed of a pair of porphyrins linked together in a so called 'face-to-face' manner. Complexes based on porphyrins are particularly attractive since they offer a near-maximum degree of complex stability and ligand inertness. There are, however, problems with many binary porphyrin molecules: (i) in general they are difficult to prepare, (ii) the high degree of similarity between the two co-ordination sites make the preparation of mixed metal complexes especially difficult, and (iii) because of the complexity, their syntheses tend to be rather inflexible with respect to subtle structural changes.

Reported here is the synthesis and preliminary characterization of a new ligand composed of a single porphyrin species and a second nonporphyrin square-planar tetradentate co-ordination site. The molecule, *meso*-α,α,α,α-tetra(*o*-nicotinamidophenyl)porphyrin (nic$_4$TPPH$_2$) (**1**) is prepared (10% yield, based on pyrrole assuming the complete conversion of all atropisomers into the α,α,α,α-isomers) by the reaction of the corresponding *meso*-α,α,α,α-tetra(*o*-aminophenyl)porphyrin[3] with a two-fold excess of nicotinoyl chloride–HCl in dichloromethane–pyridine solvent at room temperature. Only a single porphyrin (**1**) is produced in the final reaction step (as determined by high pressure liquid chromatography) which is purified by recrystallization from chloroform by the addition of ether.



(1)

Schematic representation of the structure of (**1**). Multiple bonds have been omitted for clarity.

Treating (**1**) with 2 mol of Cu(NO$_3$)$_2$·2·5 H$_2$O in acetone instantly gives the red-orange colour characteristic of Cu^{II} porphyrins. Magenta crystals are slowly formed from this solution over a period of several days. The resulting solid copper complex contains a single Cu^{II} per molecule located in the porphyrin pocket [nic$_4$TPPCu^{II}] as confirmed by both the elemental analysis† and visible spectrum (λ_{max} 542 and 413 nm). The e.s.r. spectrum obtained from the Cu^{II}–nic$_4$TPPH$_2$ solution prior to the initiation of crystallization reveals the presence of a species having a strong Cu–Cu interaction. This is evidenced by the observation of six of the seven lines in the $g_{\parallel}$ spectrum as is predicted for a triplet ($S=1$) state. This result is indicative of a bis-copper complex in which the two copper atoms interact strongly and is a phenomena that has been observed for other similar molecules.[1,4] It appears from the e.s.r. spectrum that, in solution, the bis-copper complex of (**1**) exists as the major species and the mono-copper complex is isolated apparently only because of its greatly reduced solubility.

Treatment of (**1**) with an excess of anhydrous CoCl$_2$ under N$_2$ in refluxing benzene–tetrahydrofuran yields metallic-purple crystals upon cooling. The solution spectrum in CH$_2$Cl$_2$ is typical of a metal-free porphyrin (λ_{max} 650, 592, 549, 511, and 423 nm). Elemental analysis† is consistent with the structure nic$_4$Co^{II}Cl$_2$TPPH$_2$. This would indicate that the product contains Co^{II} co-ordinated only in the pyridine pocket. This is in marked contrast to the Cu^{II} complex in which a single copper was present but in the porphyrin pocket. The reaction conditions employed would normally be quite sufficient to produce a Co^{II} porphyrin complex, but again none is observed. It is speculated that the chloride ions in the complex are co-ordinated to the cobalt atom axial to the pyridine groups. For steric reasons then, the chloride ion protruding toward the porphyrin ring may prevent the complexation of the second cobalt atom.

Finally, very recently we have prepared other metal complexes of nic$_4$TPPH$_2$. Indications are that a number of these are the respective bis-metal complexes. Also, in a few cases we appear to have succeeded in preparing some mixed-metal species.

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† Elemental analyses were within ± 0·3% of calculated values.

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