Synthesis of Polymer-Bonded Quaternary Ammonium Type Metal Porphyrins

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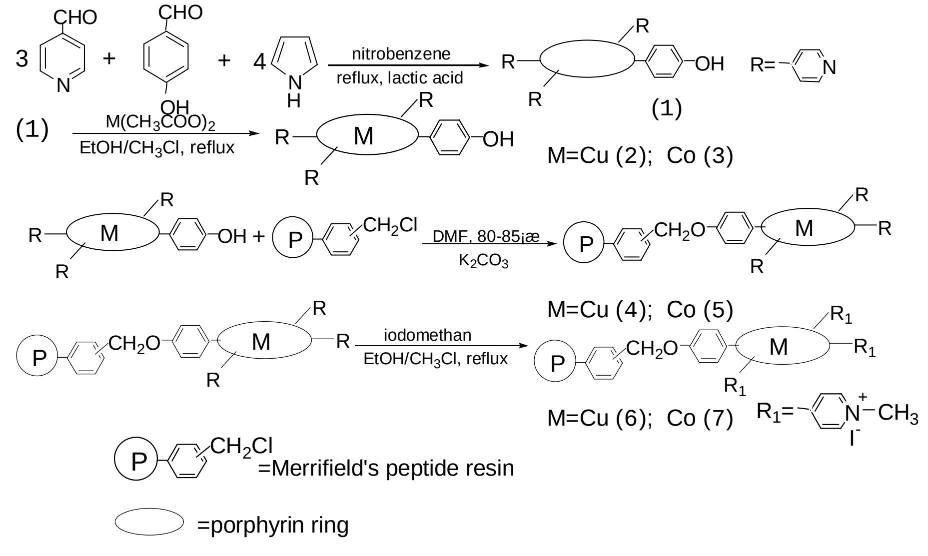
Abstract: The reaction of pyrrole with 4-hydroxybenzaldehyde and 4-pyridinecarboxaldehyde afforded new porphyrin ligand **1**. Treatment of **1** with copper(Ⅱ) acetate, cobalt (Ⅱ) acetate gave complexes **2-3** respectively. **2** and **3** reacted with Merrifield's peptide resin produced **4** and **5**. Complexes **4** and **5** reacted with methyl iodide respectively gave **6-7**. The new compounds **1-7** have been identified by ^{1}H NMR, IR, MS and UV-visible spectra, elemental analysis and AES.

Keywords: polymer-bonded, quaternary ammonium type metal porphyrin, synthesis.

Synthetic metalloporphyrin are efficient models of the cytochrome P-450 family of mono-oxygen enzymes and have been largely used as catalysts in oxidation of alkanes and epoxidation of alkenes[1]. Polymer-bonded metalloporphyrin reveal many advantages on the catalytic reaction, where the catalysts can be easily separated from the products, recovered, and reused[2]. Quaternary ammonium salts as phase transfer catalysts were wide used in aqueous-organic two-phase conditions. Unfortunately, most porphyrins, native or synthetic, are not sufficiently soluble in aqueous phase, but most of oxygen sources of those oxidation reacts, such as NaOCl, H_2O_2 are dissolved in the water phase, so their catalytic ability were limited. Pastermack and co-workers reported 5,10,15,20-tetrakis(N-methyl-4-pyridyl) porphyrin (H_2TMPyP) has excellent water-solubility in a wide range of pH's[3]. Here we report the synthesis and characterization of polymer-bonded quaternary ammonium type metalloporphyrin **6** and **7**. The three N-methyl-4'-pyridyls on the porphyrin ring gave the metalloporphyrins more opportunities reacting with oxygen sources in water phase and the high catalytic efficiency and increasing speed of epoxide reaction will be anticipated.

The porphyrin monomer **1** was prepared by literature[4]. A solution of pyrrole, 4-hydroxybenzaldehyde, 4-pyridinecarboxaldehyde and lactic acid in nitrobenzene was refluxed with stirring for 2 h. After evaporation of the solvent *in vacuo*, the residue was dissolved in solvent of ethanol:chloroform (1∶9, V/V). Column chromatograph, (silica gel, ethanol:chloroform (100∶6, V/V)) afforded the compound **1**. The solution of compound **1** and $M(CH_3COO)_2$ (M = Cu and Co) in ethanol and chloroform (100∶6, V/V) was refluxed with stirring for 2 h. The precipitate was refluxed in 40% NaOH water solution for 1 h, then filtered and washed with water to give a red solid complex **2** (and **3)**. Treatment of complex **2** (and **3**) with Merrifieldied peptide resin in DMF under N_2 at 80-85℃ for 3 h gave **4** (and **5**) respectively. Complex **6** (and **7**) was prepared by literature[5], the solution of complex **4** (and **5**) in ethanol and chloroform containing a large excess of iodomethane was refluxed at 90-100℃ for 2 days. Then filtered and cleaned by repeated rinsing with water, ethanol and the mixed solution of ethanol and chloroform respectively to give complexes **6** and **7**. The synthetic routes of complexes are listed below.

These compounds **1-7** have been identified by ^1H NMR, IR, MS and UV-visible spectra, elemental analysis and AES. Compound **1**, Anal.Calcd for $C_{41}H_{27}N_7O$: C, 77.71%; H, 4.29%; N, 15.47%. Found: C, 77.42%; H, 4.54%; N, 15.38%. ^1H NMR (δ , ppm)($CDCl_3$): 8.93 (s, 8H, H_β); 8.68-8.56 (m, 6H, 2,6-pyridine); 8.31-8.33 (m, 8H, o-hydrophenyl and 3,5-pyridine); 7.79-7.80 (m, 2H, m-hydrophenyl); -3.03 (s, 2H, NH). UV-visible Spectra λ_{max} 420 nm (Soret band). IR, ν(KBr): 3459 (O-H), 3320 (N-H), 2917 (Ph-H), 1593, 1515, 1477 (-Ph-). MS (ESI): calcd for $C_{41}H_{27}N_7O$ (M^+) 633.7, found: 633.8. Compound **2**, Anal.Calcd for $C_{41}H_{25}N_7OCu$: C, 70.83%; H, 3.62%; N, 14.09%. Found: C, 70.46%; H, 3.87%; N, 14.48%. UV-visible Spectra λ_{max} 414 nm (Soret band). IR, ν (KBr): 3451 (OH), 2920 (Ph-H), 1595, 1508, 1456 (-Ph-), 1001 (OSMB). Compound **4**, IR, ν (KBr): 1274 (Ar-O-C), 1001 (OSMB). Compound **6**, IR, ν (KBr): 1261 (C-N), 1001 (OSMB). The content of metal of complex **6** (and **7)** was examined by AES: for **6** is 0.72 mg/g, for **7** is 0.63mg/g. the analyses data of complexes **3, 5** and **7** are similar to the complexes **2, 4** and **6** respectively.



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