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Synthesis of Tetra-Schiff Base Macrocyclic Compound Containing Benzo-12-crown-4

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Abstract: Tetra-Schiff base macrocyclic compound containing benzo-12-crown-4 was synthesized *via* condensation of 2, 6-diformyl-4-methyl-phenol with 4′, 5′- diaminobenzo-12–C- 4 promoted by proton. The compound was characterized by MS, IR ^{1}HNMR spectroscopy and elemental analysis.

Keyword: Schiff base, crown, macrocyclic compound

The Robson type ligands and their transition metal complexes are of interest as mimic models of biomolecules. They are ubiquitous in nature as active sites in a variety of metalloenzymes and are playing a significant and expanding role in industrial catalyst design. So they have been prepared and extensively studied since 1970[1,2,3]. Crown ether has hydrophobicity of outer ethylene group and ordered arrangement of inner oxo atom and can coordinate alkali metals. If crown ether ring was introduced to the metal complexes of Robson type ligands, the special steric structure of crown ether or alkali metal ion coordinated crown ether ring will cause some changes of the properties of the complexes. Therefore we designed and synthesized the crownary tetra-Schiff base macrocyclic compound (H_2L). The synthetic route is shown in **Scheme 1**.

2,6-Diformyl-4-methylphenol was prepared by the method of Gagne[4]. 4′,5′-dinitrobenzo-12-crown-4 was synthesized according to the literature[5] .

4′,5′-diaminobenzo-12-crown-4 was prepared by the improved method reported by Kruse[6]. 4′,5′-dinitrobenzo-12-crown-4 3.14 g (10 mmol) was dissolved in 30 mL 2-methoxyethanol, 0.2 g Pd/C (10%) was added into the solution and then the mixture was hydrogenated at 60°C and 4.0 MPa of hydrogen pressure. The reaction was monitored by TLC (silica gel, ethyl ether : ethanol = 3 : 1). When the reaction completed, the mixture was filtered at once. The filtrate was cooled under N_2, and ashy crystals formed. The crystals were filtered and washed with cool ethyl ether, and then dried in vacuum. The yield was 1.87g (73.6%). mp 162~163°C, MS (70eV) *m/z* (%), 254 (M^+, 100), ^{1}H NMR(500 MHz, DMSO-d_6, δ ppm): 3.66~4.12 (m, 12H, 3 × OCH_2CH_2), 4.33 (s, 4H, 2 × NH_2, D_2O exchangable), 6.30 (m, 2H, C_6H_2). IR(KBr, cm^{-1})

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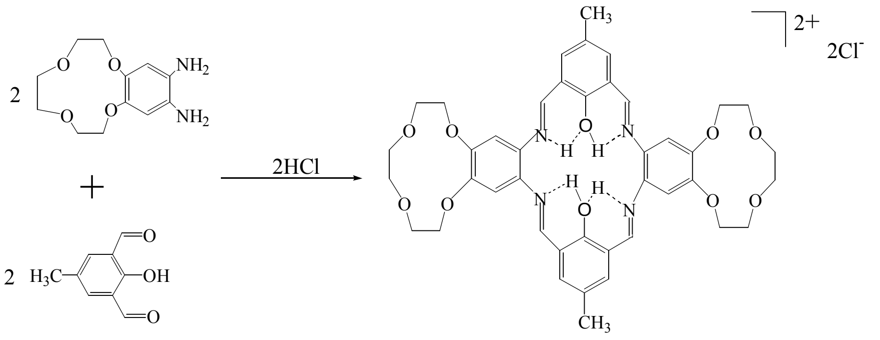
Scheme 1



υ : 3402, 3354 (NH_2), 1262, 1200 (Ar-O-C), 1134, 1100 (C-O-C). Anal. for $C_{12}H_{18}N_2O_4$ (Calcd.: C, 56.69; H, 7.09; N, 11.02; Found: C, 56.58; H, 7.11; N, 11.06).

Preparation of $H_2L \bullet 2HCl$: 0.254 g (1 mmol) of 4′,5′diaminobenzo-12-crown-4 was dissolved in 4 mL absolute methanol, then 0.1 mL concentrated hydrochloric acid and ethanol solution (30 mL) of 2, 6-diformyl-4-methylphenol (0.164 g, 1 mmol) were dropwise added slowly with stirring. After stirred for 12 h at room temperature, the dark blue precipitate was formed, the precipitate was filtered and washed with ethanol, diethyl ether, and dried in vacuum to give 0.284 g products (yield 65%). mp 222-224°C. MS(70eV) *m/z*(%), 763 (M-2HCl-1, 100); ^1H NMR (500 MHz, DMSO-d_6, δ ppm): 2.42 (s, 6H, 2 × CH_3), 3.60~4.20 (m, 24H, 6 × OCH_2CH_2O), 6.80~7.91 (m, 8H, 4× C_6H_2), 9.50 (s, 4H, 4 × CH=N), 11.20 (s, 2H, 2 × OH, D_2O exchangable); IR(KBr, cm^{-1}) υ: 3406 (OH), 1630 (C=N), 1276, 1222 (Ar-O-C), 1140, 1096 (C-O-C). Anal. for $C_{42}H_{46}Cl_2N_4O_{10}$ (Calcd.: C, 60.22; H, 5.49; N, 6.69; Found: C, 59.31; H, 5.57; N, 6.85).

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