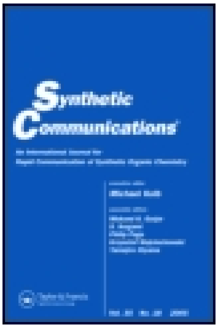

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SYNTHESIS AND CHARACTERIZATION OF NOVEL MULTIFUNCTIONAL HOST COMPUNDS. 3. β–CYCLODEXTRIN DERIVATIVES BEARING SCHIFF BASE MOIETY

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Abstract: Four novel β–cyclodextrin derivatives bearing Schiff base moiety were first synthesized by a convenient method with satisfactory yields,and the new host molecules were characterized by ^{1}H–NMR, FT–IR, FAB–MS spectra etc.

Recently, biosimulation have greatly interested chemists, they expect much of gaining novel and efficient technology and material with the aid of simulating the structure and function in biological systems through a clear understanding of the life phenomena at molecular level[1,2] Due to their doughnut–shaped structure, hydrophobic cavity and hydrophilic exterior surface, cyclodextrins(CDs) and their chemically modified derivatives can be

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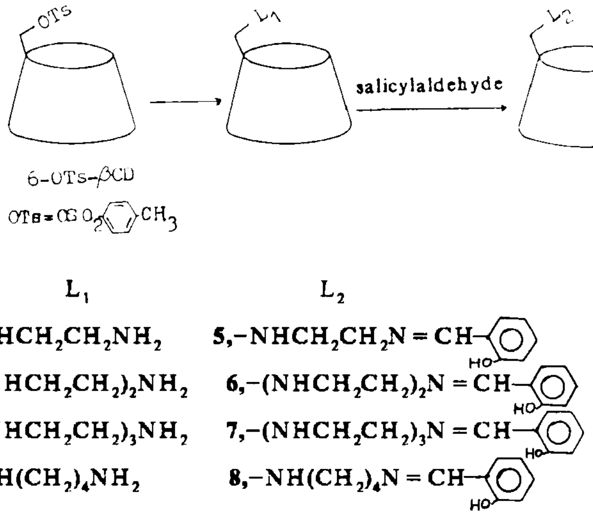

Scheme I

used as excellent hosts to form host–guest complexes with a wide variety of guest molecules[3,4], and some of them are successful enzyme models[5,6]. However, only a few studies have been published about attaching a structural subunit containing metal–binding sites to the CDs in order to mimic the activity of metalloenzymes[2,6]. In the present study we designed and synthesized a series of "multiple recognition" hosts consisting of the hydrophobic binding site of β–CD moiety and the adjacent metal coordination site of Schiff base moiety, which are shown in Scheme I.

Compounds **1,2,3,4** were synthesized in our laboratory and characterized by ^{13}C–NMR, FAB–MS spectra etc.[7]

The FT–IR spectra(especially in the region 1200— 1800cm^{-1}) of hosts **5,6,7,8** indicate that they are very different from that of

1,2,3,4 or the parent β−CD, the band around 1610 cm^{-1}reasonably reveal that a C=N bond has formed in the new host molecules, in addition, the apperance of bands around 1584, 1489 cm^{-1}(aromatic C=C stretching), 1532, 1281 cm^{-1}(phenol C−O, O−H stretching respectively) indicate the existance of schiff base moiety in the new host.

The ^{1}H−NMR spectra also suggest that a C=N bond has formed in the reaction, and the CHO group have disappeared in the target molecules, in the region δ6.60— 8.55ppm, the peaks are very similar to the characteristics of N,N′−disalicylidene ethyl enediamine. The FAB−MS spectra are also satisfactory. All these information have demonstrated that the host design and synthesis are successful, the detail analytical data will be presented in the experimental section.

The obvious evidences for the formation of their metal complexes are the FT−IR and UV−Vis spectra. For example, $Cu(ClO_4)_2$was choiced to complex with compound **5** in aqueous solution, and coordination compound **5−Cu(Ⅱ)** was obtained. Due to the coordination between Cu(Ⅱ) and Schiff base group, the band of C=N stretching moved from 1610 cm^{-1}(in compound 5) to 1603 cm^{-1}(in 5−Cu(Ⅱ)) in its infrared spectrum, while the band at 1281 cm^{-1}(phenol O−H stretching) disappeared, and the band at 1541 cm^{-1}may be assigned as phenolic C−O−Cu frequency[8], moreover, another band observed at low wavenumber 625 cm^{-1}indicated the existence of weak coordination effect between $ClO_4^-$and complexed Cu(Ⅱ) in the solid complex. The electronic spectrum of **5−Cu(Ⅱ)** showed a broad band near 625 nm (ε=122) in aqueous solution, which is considered to be associated with d−d transition of the complexed Cu(Ⅱ). The influences of the adjacent metal coordinated site on the recognition of cyclodetrin cavity to its substrates are under work.

Experimental Section

Materials; The reagents were purchased from commercial suppliers, salicylaldehyde was distilled before use.

Instruments and Methods: FAB mass spectra were recorded with a VG ZAB−HS mass spectrometer (1mA, 8KV); FT−IR spectra were taken on a Nicolet 10DX spectrometer(KBr discs) UV−Vis spectra were measured with a Shimadzu UV240 spectrophotometer; ^{1}H−NMR spectra were obtained on Varian FT−80A(80MHz) in DMSO−d_6 solution with TMS as external standard, δppm; TLC analysis were performed on 10X3cm glass plates on silca gel F_{254}(prepard ourself, eluent: 1−Propanol: AcOEt: NH_3(28%aq): H_2O,5:3:3:2, v / v)

A typical procedure for the synthesis of the new hosts is illustrated as follows: Compound 5, 0.086g (0.7mmol) salicylaldehyde was dissolved in 3ml ethyl alcohol in a flask, a solution of 0.500g (0.4mmol) **1** in 1.0ml of water was poured into the flask with vigorously shaken, and it was kept in a refrigerator overnight, a yellow precipitate formed, the mixture was extracted with 200ml ethyl ether for several times and then the aqueous layer was evaporated under vacuum to dryness, the crude product was further purified by column chromatography(sephadex G25, φ3.6X50cm) giving **5** as a yellow powder 0.3g(yield 58%). Rf 0.17(cf. 0.25 for β−CD); IR(cm^{-1}), 1584, 1489 (aromatic $V_{c=c}$), 1532, 1281(phenol V_{c-o}, V_{O-H}), 1610 ($V_{C=N}$), 1634(complexed water), 1412 (δ_{O-H}in-plane), 1155 (V^{as}_{C-O-C}glycosidic linkage), 943 (α-D-glucopyranose ring vibration), 758 (ring breathing vibration); ^{1}H-NMR(DMSO-d_6) δ, 8.44 (broad, 1H, -N=CH-), 7.25 (m, 2H aromatic hydrogen), 6.75 (m, 2H aromatic hydrogen), 4.78(broad, 7H, H_1), 2.69—3.94(m, broad, 42H,H_2—H_6; 4H,-CH_2CH_2-); FAB -MS, m/e 1282 (m+1-H_2O); Anal. calcd. for $C_{51}H_{80}O_{35}N_2 \cdot H_2O$, C47.15, H6.32, N2.16, found C46.98, H6.35, N2.23.

Compound 6, yield 87%, Rf 0.18(cf. 0.25 for β-CD); IR(cm^{-1}), 1584, 1489, 1528, 1612, 1634, 1414, 1157, 943, 758; ^{1}H-NMR(DMSO-d_6)δ, 8.38(broad, 1H, -N=CH-), 7.25(m, 2H, aromatic hydrogen), 6.78(m, 2H, aromatic hydrogen), 4.78(broad, 7H, H_1), 2.66—3.94(m, broad, 42H, H_2—H_6; 8H, -$CH_2CH_2NCH_2CH_2$-); FAB-MS: m/e 1324(M+1-3H_2O); Anal. calcd. for $C_{53}H_{85}O_{35}N_3 \cdot 3H_2O$, C46.19, H6.61, N3.05, found C46.04, H6.38, N3.12.

Compound 7, yield 72%, Rf 0.19(cf. 0.25 for β-CD); IR(cm^{-1}), 1583, 1490, 1528, 1281, 1610, 1634, 1412, 1155, 943, 758; ^{1}H-NMR(DMSO-d_6) δ, 8.44(broad, 1H, -N=CH-), 7.28(m, 2H, aromatic hydrogen), 6.81(m, 2H, aromatic hydrogen), 2.66—3.95(m, broad, 42H, H_2—H_6; 12H, -$CH_2CH_2NCH_2CH_2NCH_2CH_2$-); FAB -MS: m/e 1368(M+1-3H_2O); Anal. calcd. for $C_{55}H_{90}O_{35}N_4 \cdot 3H_2O$, C46.48, H6.76, N3.94, found C46.25, H6.46, N4,14.

Compound 8, yield 81%, Rf 0.13(cf. 0.20 for β-CD); IR(cm^{-1}), 1583, 1491, 1530, 1283, 1615, 1634, 1414, 1157, 943, 756; ^{1}H-NMR(DMSO-d_6) δ, 8.44(broad, 1H, -N=CH-), 7.23(m, 2H, aromatic hydrogen), 6.78(m, 2H, aromatic hydrogen), 4.73(broad, 7H, H_1), 2.89—3.95(m, broad, 42H, H_2—H_6), 2.75 and 1.50(broad, 8H, -$NCH_2CH_2CH_2CH_2N$-); FAB-MS, m/e 1309(M+1-4H_2O);

Anal. calcd. for $C_{53}H_{84}O_{35}N_2 \cdot 4H_2O$, C46.09, H6.67, N2.03, found C46.16, H6.42, N2.10.

Coordination Compound 5−Cu(Ⅱ), green microcrystal powder, IR (cm^{-1}): 1640, 1603, 1541, 1451, 1406, 1304, 1157, 945, 760, 625, UV−Vis (nm): 625 ($\varepsilon = 122$), 355 ($\varepsilon = 4347$), 265 ($\varepsilon = 14604$); Anal. calcd. for $C_{51}H_{80}O_{35}N_2Cu(II)ClO_4 \cdot 3H_2O$, C40.84, H5.78, N1.87, Cu4.24, found C40.87, H5.67, N2.08, Cu3.98.

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