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Preliminary communication

Preparation and properties of inclusion compound of cyclopentadienylmanganese tricarbonyl complex with a β-cyclodextrin dimer

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Abstract

The host–guest inclusion compound of cyclopentadienylmanganese tricarbonyl (guest) with β-cyclodextrin dimer (host) bridged with two 1,2-diaminoethane has been prepared as the first example of cyclodextrin dimer inclusion compounds with organotransition metal complexes and characterized by elemental analysis and IR spectra as well as thermogravimetric analysis. The manganese complex included in the dimer is thermally more stable than the free complex. ^{1}H NMR spectroscopy has established that the cyclopentadienylmanganese complex and the dimer form an inclusion compound in aqueous solution with a stability constant (β_2, 195 mol^{-2}l^2) at 22°C. The spectroscopic studies and the results of elemental analysis revealed that stoichiometry (1 : 2, host : guest) of the inclusion compound in water is identical to its stoichiometry in solid state.

Keywords: Manganese; Inclusion compound; Cyclodextrin; Carbonyl; Pentadienyl; β-cyclodextrin dimer

1. Introduction

A great number of organotransition metal complexes have been synthesized and have attracted much attention as homogeneous catalysts in organic reactions, and much effort has been paid to improve their activity and selectivity. Cyclodextrins (CDs) or their simple derivatives are comprised of six, seven, and eight glucose units (α-, β- and γ-CD, respectively), each having a slightly different hydrophobic cavity. They can form inclusion compounds with a wide varity of guest compounds via noncovalent bonds [1] and have been studied as enzyme models in biomimetic chemistry. In order to increase guest-binding ability regiospecific multifunctionalization of cyclodextrins has become increasingly important. Tabushi et al. [2] and others [3] have synthesized a few β-CD dimers linked at the C-6 carbon, and characterized the bonding of some guest molecules to β-CD dimers by high association constants as compared to the binding properties of β-CD. However, the guests studied have generally limited organic molecules, moreover to date there are only a few reports on the interaction between organometallic complexes and cyclodextrins. Breslow et al. reported high acylation rates for β-CD using ferrocene derivatives and assumed β-CD inclusion compounds with guest molecules as intermediates [4]. Harada et al. described the preparation and proposed structure of CDs inclusion compounds with ferrocene [5] or (η^6-arene)tricarbonylchromium(0) [6]. Recently, Shimada et al. reported the preparation of inclusion compounds of CDs with simple metal carbonyl complexes [7]. In our laboratory the β-CD inclusion compounds with heterocyclic [8] or cyclopentadienyl [9] manganese complexes have been investigated. Now we have attempted to prepare the inclusion compound (Fig. 1) of cyclopentadienylmanganese tricarbonyl [$MnCp(CO)_3$] with the β-CD dimer [(β-CD)$_2$(en)$_2$] bridged with two 1,2-diaminoethane and to

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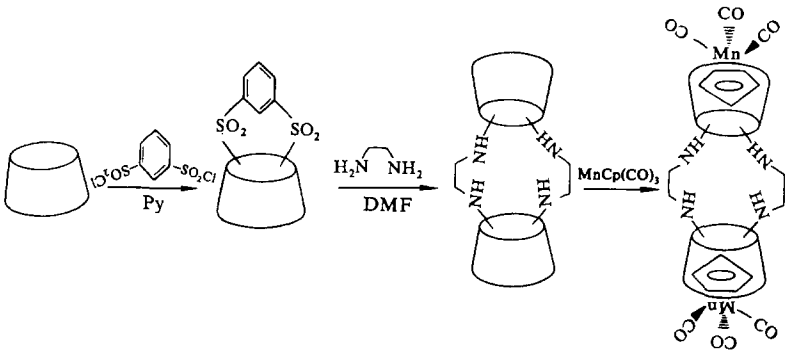

Fig. 1. Preparation and proposed structure of the β-CD dimer inclusion compound with cyclopentadienylmanganese tricarbonyl.

investigate the binding of the manganese complex by the dimer in aqueous solution.

2. Results and discussion

2.1. Inclusion compound in the solid state

The host molecule, β-cyclodextrin dimer bridged with two 1,2-diaminoethanes, has two hydrophobic binding sites and can accommodate two guest molecules, each having a hydrophobic recognition element, to form a 1:2 inclusion compound. The guest molecule, cyclopentadienylmanganese tricarbonyl, is almost insoluble in water. Cocrystallization from aqueous solution, the usual method for preparation of inclusion compounds for water-soluble compounds [10] cannot be used in this case. In the light of the previous reports by Harada [11,12,13,14,15], the title inclusion compound was prepared by adding a four-fold molar excess of fine crystals of $MnCp(CO)_3$ to a stirred aqueous solution of the β-CD dimer at 50°C. A 1:2 (host:guest) stoichiometry was determined by elemental analyses (Found: C, 45.59; H, 6.06; N, 2.13%; Calc. for $C_{104}H_{158}N_4O_{72}Mn_2$: C, 45.81; H, 5.80; N, 2.05%) and manganese contents (Found: 4.27; Calc.: 4.03%) measured by Inductivity Coupled Plasma analyses.

The solid inclusion compound was characterized by IR spectra and thermal analyses, it is thermally stable and does not liberate the included manganese complex on heating at 140°C in vacuo. Thermogravimetric analyses (Fig. 2) revealed that the unincluded manganese complex decomposes at 76°C under an argon atmosphere in the case of the free manganese complex or a 1:1 mixture of the manganese complex and the dimer, however, under the same conditions the inclusion compound of the manganese complex with the β-CD dimer is stable up to 295°C.

The results of the thermal analyses were confirmed by the IR investigation. IR spectra showed no absorption bands in the carbonyl region for the mixture after heating up to 90°C, indicating complete decomposition of the manganese complex, in contrast with clear strong absorption bands due to the carbonyl ligands at 2017 and 1911 cm^{-1} for the inclusion compound under the same conditions, suggesting that the interaction between the manganese complex and the dimer is a real inclusion phenomenon. Fig. 2 shows that the manganese complex included in β-CD or the β-CD dimer is thermally much more stable than the free complex. Comparison of the decomposition temperature indicates only a slight difference between β-CD inclusion compound and that of β-CD dimer with the manganese, suggesting that the additional β-CD as a second binding site was almost inefficient to increase thermal stability of the manganese complex.

2.2. The binding of the manganese complex by β-CD dimer in aqueous solution

Although cyclopentadienylmanganese tricarbonyl is rather insoluble in water, concentrations of the complex of the order of 10 mg ml^{-1} can be achieved at room

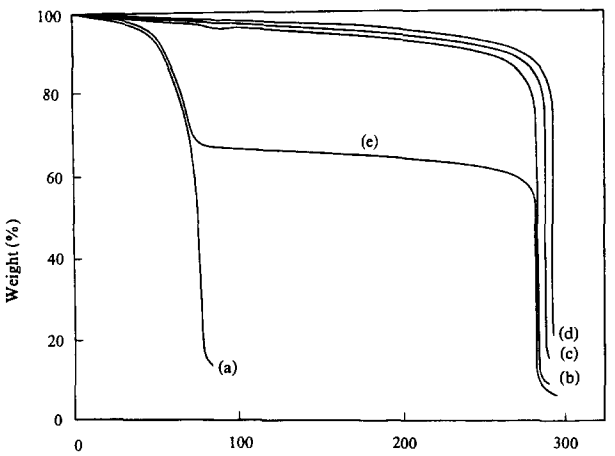

Fig. 2. Thermogravimetric curves of the free manganese complex (a), the β-CD dimer (b), the inclusion compound (c) of β-CD with the complex, the inclusion compound (d) and the mixture (e) of the dimer and the complex.

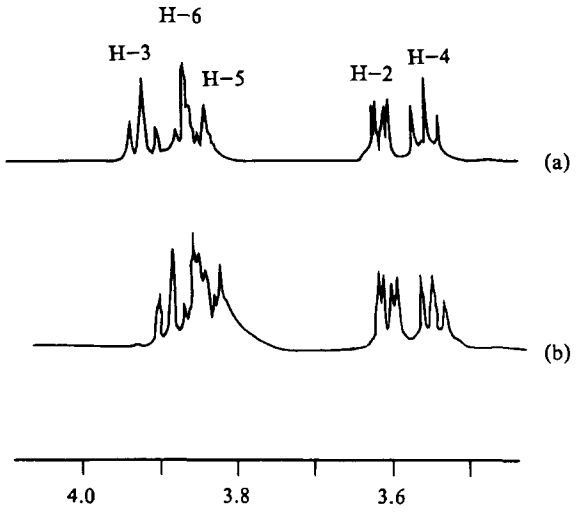

Fig. 3. The 500 MHz ^{1}H NMR spectra of (a) (β-CD)$_2$(en)$_2$, (b) (β-CD)$_2$(en)$_2$·[MnCp(CO)$_3$)]$_2$ in D_2O at concentrations of approximately 3.2 mmol l^{-1}.

temperature in an aqueous solution of the β-CD dimer. Qualitative evidence for host–guest binding comes from ^{1}H NMR spectroscopic investigations performed on [β-CD)$_2$(en)$_2$-MnCp(CO)$_3$] system in D_2O at 22°C. ^{1}H NMR spectra of the β-CD dimer were measured in the presence and absence of MnCp(CO)$_3$. It was found that all the proton signals due to the host molecule shifted upfield in the presence of MnCp(CO)$_3$ (Figs. 3 and 4). The upfield shift of the signal due to H-3 inside the cavity of the host was the most prominent, followed by those due to H-5 and H-6 inside the cavity. The upfield

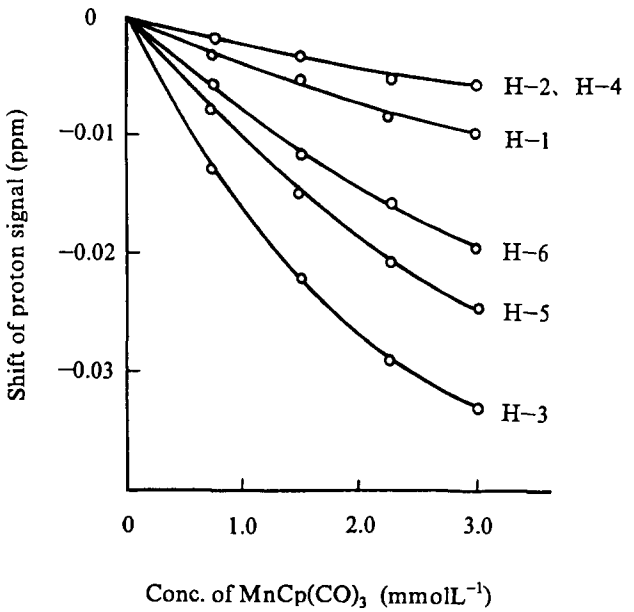

Fig. 4. Induced ^{1}H NMR chemical shifts of β-CD dimer (2.5 mmol l^{-1}) in the presence of the manganese complex.

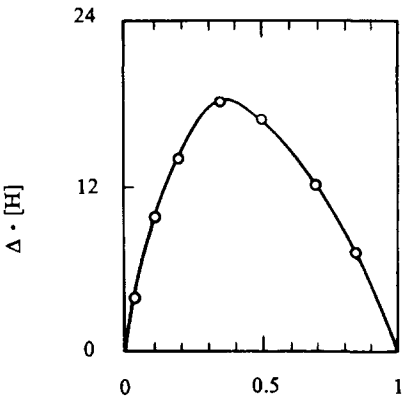

Fig. 5. Continuous variation plot (Job plot) for H-3 proton of the dimer.

shifts of the signals due to protons outside the cavity was slight. It is believed that these upfield shifts of the host proton signals result mainly from the magnetic field of the cyclopentadienyl π cloud. The proton signals of the cyclopentadienyl ring of the manganese complex (2.0 mmol l^{-1}) shift downfield (0.09–0.025 ppm) after adding the dimer (from 2.5 to 6.5 mmol l^{-1}), which can be considered to have occurred mainly because protons of the cyclopentadienyl ligand contact strongly with the atoms lying on the inner surface of a double β-CD cavity, namely by the steric compression effect [16].

The stoichometry of the inclusion compound in aqueous solution was established by the continuous variation method (Job plot) [17] which was used to follow the changes in chemical shift of proton H-3 of the dimer (Fig. 5). The overall concentration of host (H) and guest (G) was kept constant ($H_0 + G_0 = 7.2$ mmol l^{-1}), and the ratio $r = H_0/(H_0 + G_0)$ was varied from 0 to 1 (H_0 and G_0 are the total concentrations of host and guest, respectively). The quantity $\Delta \cdot$ [H] was plotted against r (Δ is the difference between the chemical shift of free H and observed value for a given ratio r).

The plot for the (β-CD)$_2$(en)$_2$-MnCp(CO)$_3$ system showed a maximum at $r = 0.33$ which corresponds to a 1 : 2 stoichiometry within the range of concentrations investigated. The result indicates that two MnCp(CO)$_3$ molecules participate in the binding of two β-CD units of the dimer, respectively.

In 500 MHz ^{1}H NMR spectra of the dimer and the dimer inclusion compound distinct peaks are not observed for a bound and a free form, therefore the bound and free forms rapidly exchange on the NMR time scale. Consider the following equilibrium expressions:

$$H + 2G = HG_2 \quad (1)$$

$$H + G = HG \quad (2)$$

$$HG + G = HG_2 \quad (3)$$

If in a solution the primitive concentration of the host is x, the primitive concentration of the guest is $2x$, m and n represent equilibrium concentration of 1:1 inclusion compound (HG) and 1:2 inclusion compound (HG_2) respectively, then the stability constant (β_2) of the 1:2 inclusion compound in aqueous solution was estimated by the following approximate method.

$$\beta_2 = n \cdot (x - m - n)^{-1} \cdot (2x - m - 2n)^{-2} \quad (4)$$

For a given proton, the observed chemical shift (δ_{obs}) for the resonance of the probe (H-3 in the dimer) of the (β-CD)$_2$(en)$_2$-MnCp(CO)$_3$ system in D_2O at 22°C is weighted by δ_H, δ_m and δ_n which represent the chemical shift for the probe protons in free host, 1:1 inclusion compound (HG) and 1:2 inclusion compound (HG_2), respectively,

$$\delta_{obs} = (x - m - n) \cdot x^{-1} \cdot \delta_H + m \cdot x^{-1} \cdot \delta_m + n \cdot x^{-1} \cdot \delta_n \quad (5)$$

As a matter of fact the host molecules between two inclusion states can reasonably be considered as mangnetically equivalent [18], that is to say:

$$\delta_m \equiv \delta_n \equiv \delta_w \quad (6)$$

If Δ and Δ_0 are defined by Eq. 7 and 8, respectively,

$$\Delta = \delta_{obs} - \delta_H \quad (7)$$

$$\Delta_0 = \delta_w - \delta_H \quad (8)$$

As has been indicated that in D_2O solutions the inclusion compounds exist mainly in form of HG_2, therefore m can be neglected. Combining and rearranging Eqs. (4)–(8) give Eq. 9:

$$\Delta = \Delta_0 - (\Delta/x^2)^{1/3} \cdot (\Delta_0^2/4\beta_2)^{1/3} \quad (9)$$

Plots of Δ against $(\Delta/x^2)^{1/3}$ gives a good straight line, as required by Eq. 9 from which β_2 value of 195 mol^{-2} l^2 was calculated. Compared with β-CD (K value, the association constant of β-CD inclusion compound with the manganese complex, of 110 mol^{-1} l), the β-CD dimer which has a second β-CD as an additional site showed a considerable enhancement of binding ability to cyclopentadienylmanganese tricarbonyl, demonstrating the second hydrophobic binding site participate in the binding of the other manganese complex. Since proton H-3 indicates a greater shift increase with respect to the H-6 and H-5 upon complexation, a fact suggesting that the manganese complex only partially penetrated the cavity from the large-diameter side of CD. Compared with the carbonyl moiety [6], the cyclopentadienyl group of the manganese complex was the preferential one which penetrated in the hydrophobic cavity of the dimer. According to a consideration with CPK models the proposed structure for the β-CD dimer inclusion compound with cyclopentadienylmanganese tricarbonyl is shown in Fig. 1.

3. Experimental section

3.1. General

β-Cyclodextrin of a reagent grade obtained from Suzhou Monosodium Glutamate Factory was recrystallized twice from water and dried over P_4O_{10} for 24 h at 110°C in vacuo before use. Pyridine (Py) was freshly distilled and collected over solid KOH. Dimethylformamide (DMF) was purified by refluxing over CaH_2 for 12 h and then distilled under reduced pressure. The cyclopentadienylmanganese tricarbonyl obtained from Aldrich Chemical Company, Inc. was used without further purification. Other reagents are all analytical pure grade. Elemental analysis was made using a Perkin-Elmer 240 C elemental analyzer. Inductivity Coupled Plasma analysis of manganese contents was made using a Jarrel-ASH 1100 quantometer. IR spectra were recorded on a Nicolet 170 SX FT spectrometer and ^1H NMR spectra in D_2O were measured with a Bruker 500 MHz spectrometer at 22°C. Tetramethylsilane was used as an external reference. Thermogravimetric analysis was made with a Shanghai ZRY-1 thermal analyzer.

3.2. Preparation of the β-CD dimer

m-Benzenedisulfonyl chloride was prepared by treatment of sodium *m*-benzenedisulfonate with PCl_5 according to the described procedure [19]: mp 62–63°C (Ref. [19] mp 63°C). *m*-Benzenedisulfonyl capped β-CD was prepared by adding dropwise 4.3 g (16 mmol) *m*-Benzenedisulfonyl chloride dissolved in 150 ml of dry pyridine to a stirred dry pyridine solution (1350 ml) of dry β-CD(60 g, 53 mmol), purified by silica gel column chromatography using CH_3CN–H_2O (1:1) as an eluent: IR(KBr) 1372, 1160, 816, 684 cm^{-1}; ^1H NMR(Me_2SO-d_6) 2.79–4.70 (m, 61H), 4.70–4.98 (m, 7H), 7.90–8.44 (m, 4H) [20]. The β-CD dimer bridged with two 1,2-diaminoethane, was synthesized by reacting a slight excess of *m*-benzenedisulfonyl capped β-cyclodextrin (0.86 g, 0.64 mmol) with 1,2-diaminoethane (0.04 ml, 0.60 mmol) in DMF (80 ml) at 88°C for 60 h, and purified by ion-exchange column chromatography [2]. A paper chromatogram (10% NH_4OH–EtOH–BuOH, 5:10:2) of the dimer exhibited only a clear spot of R_f 0.56. The satisfactory element analysis (Found: C, 45.15; H, 6.61; N, 2.84% Calc. for $C_{88}H_{148}N_4O_{66}$: C, 45.58; H, 6.44; N, 2.42%) and the NMR spectra [^1H NMR δ3.4 (16H,N–CH_2); 3.5–4.7 (76H); 5.4 (14H, C_1H), ^{13}C NMR 100.51 (C_1); 79.71

(C_4); 71.76 (C_3); 70.42 (C_2, C_5); 58.69 (C_6); 47.63 (C–NHR)] of the β-CD dimer were obtained.

3.3. Preparation of inclusion compound

The inclusion compound of cyclopentadienylmanganese tricarbonyl with the β-CD dimer was prepared by adding a fine crystal of the manganese complex (0.20 g, 1.0 mmol) to an aqueous solution (50 ml) of the dimer (0.58 g, 0.25 mmol) at 50°C with stirring under N_2 atmosphere. The product was filtered off, washed thoroughly with water to remove any remaining dimer and dried in vacuo. Unincluded manganese complex was removed by washing the residue with tetrahydrofuran and vacuum drying. During this process, the enclosed manganese complex was not liberated from the dimer cavity.

Acknowledgements

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