NOTE

Complexation of Dicarboxylic Acids Containing Ferrocene Nucleus with Aluminium Ion[†]

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Abstract: IR and ²⁷Al NMR spectra of 1,1'-bis(ω -carboxyalkanoyl)ferrocenes in the presence of metal ions indicated complexation of 1,1'-bis(3-carboxypropanoyl)ferrocene and 1,1'-bis(5-carboxypentanoyl)ferrocene with aluminium ion.

Key words: ²⁷Al NMR, IR, Metal-complexation, ferrocene derivative

1 Introduction

One of the interesting features of ferrocene derivatives is the rotation of the cyclopentadienyl (Cp) rings. For the unsubstituted ferrocene, its two Cp rings in the molecule freely rotate around the Cp-Fe-Cp bond axis in the solution (1). The ferrocene nucleus with substituents A and B on the different Cp rings would be found as an axis bonding A and B.

In a previous study (2), the authors carried out hydrolysis of 1,1'-bis[ω -(methoxycarbonyl)alkanoyl]ferrocenes. The relationship between the reactivity and specific structure was then discussed. As a result, for the compounds which have the same 1- and 1'-substituents, the k_1 and k_2 values are different. This may be caused by the electrostatic interaction between the two carbonyl groups.

In this study, the interaction between the carboxyl groups and metal ions, and the conformation of the ferrocene nucleus were discussed from the spectral data of the carboxylic acids prepared from 1,1'-bis[ω -(methoxycarbonyl)alkanoyl]ferrocenes by hydrolysis.

2 Experimental

The 1,1'-bis(3-carboxypropanoyl) ferrocene (**1**), 1,1'-bis(5-carboxypentanoyl)ferrocene (**2**) and 1,1'-bis(9-carboxynonanoyl)ferrocene (**3**) were prepared by known methods (3). The compounds were identified by ¹H NMR, IR, and mass spectra as described in the previous paper (2).

The IR spectra were measured with a Shimadzu FT-IR 8400 spectrometer by use of nujol mull method. ²⁷Al NMR spectra were recorded with a JEOL A-400 spectrometer operating at 104 MHz. The pulse width was 20 μ s, and the scan time was 400. The measurements were carried out for a 5% (w/w) methanol-d₄ solution at ambient temperature using 5 mm ϕ sample tubes. The chemical shifts were referenced to AlCl₃ as the external reference.

3 Results and Discussion

The IR spectra of compounds **1-3** in addition to benzoic acid and phthalic acid were measured in the presence of metal ions. The carbonyl stretching wavenumbers of the carboxyl groups are shown in **Table 1**. In

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this table, the differences in the wavenumbers in the absence and presence of the metal ions are also shown. Na^+ did not make a shift. For benzoic acid, no differences were observed when the ions were added. These ions would not coordinate to this acid. However, for phthalic acid, small shifts were observed when the ions except Na^+ were added (**Table 1**). This would be caused by the decrease in the double bond character of the carbonyl groups due to the coordination of these ions to the carbonyl oxygens (4). The order of the magnitudes of the shifts by the alkaline-earth metal ions was $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+}$. Namely, this order shows the coordination facility to the carbonyl oxygens. This order is similar to that of the complex-forming ability of the alkaline-earth metal ions (5).

The IR spectra of the ferrocene derivatives **1** and **2** in the presence of the alkaline-earth metal ions or aluminium ion showed the lower shifts in the wavenumber for the phthalic acid. Namely, an interaction between these ferrocene derivatives and the ions is suggested. In contrast, for the ferrocene derivative **3**, which has longer methylene chains, the shift was not observed in the presence of ions. As mentioned in the previous paper (2), for the conformations in which the 1- and 1'-substituents are adjacent, the two terminal carbonyl groups are able to approach with more difficulty than for the lower member compounds **1** and **2**. As a result, the interaction mentioned above would not occur in compound **3**. From the results that only compounds **1** and **2** form complexes, these compounds act as bidentate ligands in which the two carbonyl groups are coordination points.

The ^{27}Al -NMR spectra were measured in order to examine the coordination of the aluminium ion to the

ferrocene derivatives. The spectra of AlCl_3 in the presence of derivatives **1** and **3** are shown in **Fig. 1**. The chemical shifts of the ^{27}Al NMR spectra are summarized in **Table 2**. The chemical shift of AlCl_3 was defined as 0. When AlCl_3 was added to phthalic acid at the equimolar ratio, a new higher field peak appeared at -6.4 ppm (6). The new peak became relatively larger at the molar ratio of 5 (AlCl_3 /substrate). It seems that the lower field peak is due to AlCl_3 and the higher one is due to the complex between the phthalic acid and AlCl_3 . The ^{27}Al chemical shifts are governed by a diamagnetic term; the observed higher field shifts should be caused by the interaction between the Al atom and carbonyl oxygen having an electron donating facility (7).

For the ferrocenes, when AlCl_3 and compound **1** were mixed, a higher field peak was observed at -6.7 ppm (**Fig. 1**). This peak would be due to the complex between AlCl_3 and compound **1** as found in the phthalic acid complex. This result supported the fact that derivative **1** forms a complex with Al^{3+} based on the IR measurement. For compound **3**, only one major peak due to AlCl_3 appeared, while a higher field peak was very weak (**Fig. 1**). Namely, compound **3**, which has longer methylene chains, would not or little form a complex with AlCl_3 .

In summary, based on the IR and ^{27}Al NMR spectra, 1,1'-bis(3-carboxypropanoyl)ferrocene (**1**) and 1,1'-bis(5-carboxypentanoyl)ferrocene (**2**), which have shorter methylene chains, act as bidentate ligands to form complexes with the metal ions. This result means that the two Cp rings of these ferrocene derivatives are restricted to rotate around the Cp-Fe-Cp bond axis by forming complexes with these metal ions. However, the

Table 1 IR Stretching Wavenumbers of Carboxy Groups.

Compounds	Wavenumber (cm^{-1})					
	none	Mg ^a	Ca ^a	Ba ^a	Al ^a	Na ^a
Benzoic acid	1670	---	---	---	1669(-1) ^b	1669(-1) ^b
Phthalic acid	1672	1635(-37) ^b	1647(-25) ^b	1654(-18) ^b	1650(-22) ^b	1672(0) ^b
Compound 1	1673	1662(-11) ^b	1656(-17) ^b	1662(-11) ^b	1663(-10) ^b	1673(0) ^b
Compound 2	1667	1657(-10) ^b	1657(-10) ^b	1660(-7) ^b	1658(-9) ^b	1667(0) ^b
Compound 3	1678	1678(0) ^b	1678(0) ^b	1678(0) ^b	1678(0) ^b	1678(0) ^b

a The sample were yielded by mixing of the acids and the corresponding hydroxides in methanol followed by evaporation of the solvent.

b The shifts in the wavenumbers in the absence and presence of the metal ions.

Fig. 1 ^{27}Al -NMR AlCl_3 Alone (left), in the Presence of Compound **1** (middle) and Compound **3** (right).

Table 2 ^{27}Al -NMR Chemical Shifts of AlCl_3 in the Presence of Carboxylic Acids.

Samples	Ratio	Chemical shifts (ppm)	
AlCl_3		0	
AlCl_3 / Benzoic acid	1 : 1	0	
AlCl_3 / Phthalic acid	1 : 1	0	-6.4
AlCl_3 / Phthalic acid	5 : 1	0	-6.4
AlCl_3 / Compound 1	1 : 1	0	-6.7
AlCl_3 / Compound 3	1 : 1	0	

metal ions would not coordinate to the 1,1'-bis(9-carboxynonanoyl)ferrocene (**3**).

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