Article

Ferrocene-Containing Pseudorotaxanes in Crystals: Aromatic Interactions with Hammett Correlation

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Abstract: Single crystals of pseudorotaxanes, [(FcCH2NH2CH2Ar)(DB24C8)][PF6] [DB24C8 = dibenzo [24]crown-8, Fc = Fe(C5H4)(C5H5), Ar = -C6H5-3,4-Cl2, -C6H5-3,4-F2, -C6H4-4-F, -C6H4-4-Cl, -C6H4-4-Br, -C6H3-3-F-4-Me, -C6H4-4-I] and [[FcCH2NH2CH2C6H1-4-Me(DB24C8)][Ni(dmit)]2 (dmit = 1,3-dithiole-2,4,5-dithiolate), were obtained from solutions containing DB24C8 and ferrocenyl-methyl(aryl)methylammonium. X-ray crystallographic analyses of the pseudorotaxanes revealed that the aryl ring of the axle moiety and the catechol ring of the macrocyclic component were at close centroid distances and parallel or tilted orientation. The structures with parallel aromatic rings showed correlation of the distances between the centroids to Hammett substituent constants of the aryl groups.

Keywords: pseudorotaxane; aromatic interaction; crystal structure; Hammett constants

1. Introduction

Rotaxanes and pseudorotaxanes have been investigated as supramolecules with unique structures, having macroyclic molecules threaded by axle molecules [1–9]. Their stimulus-response behavior has been applied to molecular shuttles [10–18] and molecular elevators [19] in solutions and molecular muscles in both the solid state and in solution [20–23]. Further applications of the rotaxanes include catalysis [24–28], functional polymeric materials [29–32], amphiphilic materials [33–36], and nanometal precursors [37]. Pseudorotaxanes have an axle component whose end groups are smaller than the size of the central hole of the macrocyclic component. Intermolecular interaction, such as hydrogen bonding and aromatic interaction, stabilizes the interlocked structure of the pseudorotaxanes. Dibenzo-24-crown-8 (DB24C8) forms various pseudorotaxanes and rotaxanes with dialkyl- or diarylammonium because they are bound by multiple N–H···O hydrogen bonds between the NH2+ group and the oxygen atoms. X-ray crystallographic studies of the pseudorotaxane of DB24C8 and dibenzylammonium, [[(PhCH2)2NH2(DB24C8)][PF6]], revealed interaction between the macrocyclic and axle components [38,39]. The pseudorotaxane contained multiple N–H···O hydrogen bonds between the NH groups of the axle component and O atoms of the macrocyle. One of the two crystallographically independent pseudorotaxanes was stabilized not only by the hydrogen bonds but also by π–π interaction between a Ph group of the axle component and a catechol group of the macrocyle. The two aromatic groups had parallel orientation and close positions with a...
centroid distance of 3.79 Å. Such double stabilization was observed in many rotaxanes and pseudorotaxanes of DB24C8 and bis(arylmethyl)ammonium [40–43].

In the last few decades, we have investigated structures and properties of the crystalline pseudorotaxanes of DB24C8 and ferrocenylmethyl(arylmethyl)ammonium, [(FcCH₂NH₂CH₂C₆H₄-4-Me)(DB24C8)][EFe₆] (E = P, As) [44–50]. The pseudorotaxanes caused the crystalline phase transition upon heating and photo-irradiation. Related crystalline supramolecules were reported to exhibit new stimulus–response behavior [51–54]. Scheme 1 shows two structures of the pseudorotaxane of DB24C8 with ferrocenylmethyl(4-methylphenyl)methylammonium in the crystals. The pseudorotaxane with the PF₆⁻ counter anion was supported by multiple N-H⋯O hydrogen bonds, π–π interaction between the 4-methylphenyl group and a catechol group, and C(Cp)−H⋯π interaction between the ferrocenyl group and the other catechol group (Scheme 1a, α-form). The distance and angle of the catechol ring and p-methylphenyl ring was determined to be 3.71 Å and 6.2°, respectively. The pseudorotaxane with AsF₆⁻ anion preferred the structure with C⋯H−π interaction between the 4-methylphenyl group of the axle component and a catechol group (Scheme 1b, β-form). Heating crystals of [(FcCH₂NH₂CH₂C₆H₄-4-Me)(DB24C8)AsF₆] above 128 °C caused thermal crystalline phase transition from α-form to β-form. Recent studies revealed that the crystalline phase transition temperature of the crystals was influenced largely by size of the counter anions [47,50].

![Scheme 1](image)

**Scheme 1.** Typical structures of pseudorotaxane of DB24C8 and (ferrocenylmethyl)-(4-methylphenylmethyl) ammonium.

In solution, the pseudorotaxanes of DB24C8 and benzyl(arylmethyl)ammonium, [(ArCH₂(PhCH₂)NH₂)(DB24C8)][PF₆] have been reported to show different stabilities, depending on the substituents on the aromatic groups of the axle component [55]. However, there have been no reports on relevance of the crystalline structures of such (pseudo) rotaxanes to the substituents of the aromatic group of the arylmethylammonium axle component. Here we report the crystal structures of pseudorotaxanes composed of DB24C8 and ferrocenylmethyl(arylmethyl)ammonium and show the effect of the aryl group on the molecular structures of the pseudorotaxanes. This study focuses on relative positions and orientation of the neighbouring aromatic groups of the axle and cyclic components in the α-form pseudorotaxane crystals.

2. Results and Discussion

Mixing DB24C8 with ferrocenylmethyl(arylmethyl)ammonium in solution caused crystal growth of the corresponding pseudorotaxanes. Their structures were determined by X-ray crystallography (vide infra). The reaction of DB24C8 with ferrocenylmethyl(arylmethyl) ammonium formed the corresponding pseudorotaxanes, 1a–1g, as crystals, as shown in Equation (1). Similar pseudorotaxanes with Ph, C₆H₄-4-Me, and C₆H₄-4-OMe groups in the axle component, 1h–1i, were reported previously [46–48]. Counter anion exchange of [(FcCH₂NH₂CH₂C₆H₄-4-Me)][PF₆] by [Ni(dmit)₂]⁻ (dmit = 1,3-dithiole-2-4,5-dithiolate) and subsequent addition of DB24C8 formed [(FcCH₂NH₂CH₂C₆H₄-4-Me)(DB24C8)][Ni(dmit)₂] (1i–Ni). X-ray crystallographic study showed the pseudorotaxane structure with [Ni(dmit)₂]
counter anion, although IR measurement and elemental analyses of the crystalline product were unsuccessful.

Figure 1a shows structure of pseudorotaxane 1d with a chlorophenyl group in the axle component. The ammonium hydrogens, H1 and H2, are at close positions to the oxygen atoms of DB24C8 (N1–H1⋯O2: 2.216 Å, N1–H1⋯O3: 2.240 Å, N1–H2⋯O1: 2.537 Å, N1–H2⋯O8: 2.368 Å), suggesting N–H⋯O hydrogen bonds. The cyclopentadienyl ligand forms a C–H⋯π interaction (3.09 Å) with a C6H4 ring of DB24C8. The distance between the centroid of phenylene ring A of the axle component and that of the catechol ring B of DB24C8 (d, Å) and the angle formed by the aromatic planes (θ, °) are 3.70 Å and 5.26°, respectively. Thus, the structure of pseudorotaxane 1d belongs to the α-form of Scheme 1.

Figure 1. X-ray structures of pseudorotaxanes. (a) 1d, (b) 1c, and (c) 1i-Ni. The atoms are shown with 50% probabilities. Atoms of the anion and hydrogen atoms are omitted for simplicity.

Pseudorotaxane 1c has two aromatic groups A and B with the orientation close to orthogonal, suggesting C-H⋯π interaction between the aromatic groups A and B, as shown in Figure 1b. The structure is similar to 1i above the crystalline phase transition temperature and belongs to β-form in Scheme 1. Pseudorotaxane 1i-Ni contains the 4-methylphenyl group of the axle component and a phenylene group of a catechol group in parallel fashion, as shown in Figure 1c. Previous crystallographic studies of 1h, 1i, and 1j showed that multiple C-H⋯F interactions between DB24C8 and PF6− impart the relative stability of α- to the β-form [46,47,50]. Figure 2 depicts interaction of the cationic pseudorotaxane with [Ni(dmit)2]− anion of 1i-Ni, which differs largely from that of pseudorotaxane 1i with PF6− anions.
Figure 2. Contacts between the cationic rotaxanes and [Ni(dmit)]$^2^-$ of 1i-Ni.

Table 1 summarizes synthesis and structures of the ferrocene-containing pseudorotaxanes, [(FcCH$_2$NH$_2$CH$_2$Ar)(DB24C8)][PF$_6$] (1a–1j) and [(FcCH$_2$NH$_2$CH$_2$Ar)(DB24C8)] [Ni(dmit)$_2$] (1i-Ni). The IR peaks of the symmetric and asymmetric vibration of ammonium N–H bonds of 1a–1d, 1f, 1g (3065–3080, 3166–3195 cm$^{-1}$) were observed at lower wavenumbers than those of starting ammonium, 2a–2g (3233–3236 and 3262–3268 cm$^{-1}$), due to the hydrogen bonding between the ammonium and oxygen atoms of DB24C8.

Table 1. Crystal synthesis of pseudorotaxanes, 1a–1j.

| Pseudorotaxane | End Group of Axle Component (Hammett Const.) | Yield(%) | Structure | N⋯O distance/Å | v(N–H)/cm$^{-1}$$^a$ |
|----------------|----------------------------------------------|----------|-----------|----------------|-------------------|
| 1a             | -C$_6$H$_2$-3,4-Cl$_2$                        | (0.60)   | 10%       | α             | 3.058 3.011 3060 (3233) 3185 (3262) |
| 1b             | -C$_6$H$_2$-3,4-F$_2$                        | (0.40)   | 57%       | β             | 2.975 2.840 3066 (3233) 3163 (3262) |
| 1c             | -C$_6$H$_4$-4-F                              | (0.34)   | 49%       | β             | 2.966 2.873 3077 (3236) 3165 (3262) |
| 1d             | -C$_6$H$_4$-4-Cl                             | (0.23)   | 74%       | α             | 3.088 2.949 3069 (3235) 3187 (3266) |
| 1e             | -C$_6$H$_4$-4-Br                             | (0.23)   | 85%       | α             | 3.092 2.943 3069 (3233) 3187 (3265) |
| 1f             | -C$_6$H$_3$-3-F-4-Me                         | (0.17)   | 41%       | α             | 3.062 3.006 3067 (3233) 3166 (3262) |
| 1g             | -C$_6$H$_4$-4-I                             | (0.18)   | 69%       | α             | 3.070 2.984 3065 (3235) 3195 (3268) |
| 1h$^b$         | -Ph                                          | (0.00)   |           | β             | 2.941 2.857 3065 (3236) 3156 (3262) |
| 1i$^c$         | -C$_6$H$_4$-4-Me                            | (–0.17)  |           | α             | 3.159 3.074 3067 (3250) 3171 (3225) |
| 1i-Ni          | -C$_6$H$_4$-4-Me                            | (–0.17)  |           | α             | 3.114 3.021 3065 (3235) 3195 (3268) |
| 1j$^d$         | -C$_6$H$_4$-4-OMe                           | (–0.27)  |           | α             | 2.995 2.997 3065 3195 |

$^a$ Wavenumber of the axle molecule is shown in parenthesis. $^b$ Ref. [47]. $^c$ Refs. [44,45]. $^d$ Ref. [55].

The pseudorotaxane crystals of 1i in α–form and in β–form were reported to have different conformation of the axle molecule and co-conformation of the axle and macrocyclic molecules (orientation of the axle molecule within the pseudorotaxane framework) [50]. The rotaxanes in α–form (1a, 1d–1i) and those in β–form (1b, 1c, 1h) in Table 1 showed different wavenumbers of the IR peaks due to $\nu$$_{as}$ vibrations of the NH$_2$ group, 3184 cm$^{-1}$ on average for 1a and 1d–1i and 3161 cm$^{-1}$ on average for 1b, 1c, and 1h. The distances between N1 and O2 atoms of 1a and 1d–1i, 3.079 Å on average, were longer than those of 1b, 1c, and 1h (2.960 Å on average). Thus, these spectroscopic and structural parameters relating to the N–H⋯O hydrogen bonds differ clearly between the crystals of α–form and those of β–form. Table 2 summarizes relative positions and orientations of two aromatic planes A and B of the pseudorotaxanes in the crystalline state. The two aromatic planes of α–form were almost parallel in the structures with tilt angles, in the range of 3.65–7.94°. Distances between centroids of aromatic planes A and B, are in the range of 3.573–3.779 Å.
Both values are much smaller than the corresponding values of pseudorotaxanes in β-form, 1b, 1c, and 1h.

Table 2. Centroid distance and dihedral angles between the two aromatic groups in the axle and cyclic components.

| Pseudorotaxane A Ring | Structure | Relative Positions of Two Aromatic Groups |
|-----------------------|-----------|------------------------------------------|
|                        |           | Centroid Distance, d/Å | Dihedral Angle, θ/° | Face-to-Face Dimension/Å |
| 1a                    | -C₆H₃-3,4-Cl₂ | α | 3.553 | 3.65 | 3.376  |
| 1b                    | -C₆H₃-3,4-F₂  | β | 4.850 | 122.01 | –   |
| 1c                    | -C₆H₄-4-F    | β | 5.140 | 121.78 | –   |
| 1d                    | -C₆H₄-4-Cl   | α | 3.702 | 5.26 | 3.416  |
| 1e                    | -C₆H₄-4-Br   | α | 3.694 | 5.00 | 3.394  |
| 1f                    | -C₆H₃-3-F-4-Me | α | 3.640 | 6.59 | 3.413  |
| 1g                    | -C₆H₄-4-I    | α | 3.710 | 6.71 | 3.435  |
| 1h a                   | -Ph        | β | 5.128 | 57.61 | –   |
| 1l a                   | -C₆H₄-4-Me  | α | 3.710 | 6.20 | 3.430  |
| 1l-Ni                | -C₆H₄-4-Me  | α | 3.665 | 4.59 | 3.398  |
| 1j a                   | -C₆H₄-4-OMe | α | 3.779 | 7.94 | 3.529  |

* Data were taken from the results in refs. [44–47,56].

Figure 3 shows Hammett plots of structural parameters of crystalline pseudorotaxanes with α-form, 1a, 1d–1g and 1l–1j. The distances between centroids (Figure 3a) and dihedral angles (Figure 3b) of aromatic groups A and B were plotted against the Hammett constants, α, of A [56]. Hammett constants of disubstituted aromatic group in 1a and 1f were calculated by assuming additivity of Hammett constants [57,58]. Linear relationships were observed for d and θ values to Hammett constants, and σ-values were calculated as −0.21 and −4.1, respectively. Thus, aromatic group A with a larger σ-value was positioned at a closer position to aromatic group B with a smaller dihedral angle. Coefficients of determination of the plots in Figure 3a,b were similar (R² = 0.76 and 0.73), suggesting that parameters d and θ were correlated with each other. Attempts to plot averaged distances between aromatic planes of A and B to Hammett constants resulted in lower correlation than that between d and θ. The two aromatic planes were almost parallel in the structures but had slight differences in the structural parameters. The d and θ values of pseudorotaxanes were increased by electron-donating substituents (negative σ values) of the terminal aryl group of the axle component.

![Figure 3](image_url)

Figure 3. Hammett correlations of (a) d and (b) θ to σ. Hammett constants were taken from ref. [56] by assuming their additivity.

Centroid distances of the pseudorotaxanes with monosubstituted aromatic groups A, such as 1d, 1e, 1g, 1l, and 1j, were plotted against R⁺ constants in order to estimate the
contribution of the resonance effect for the Hammett plots in Figure 3. Centroid distance of pseudorotaxane 1j with OMe group at the 4-position of A (3.779 Å) is much longer than other pseudorotaxanes with Cl, Br, I, and Me groups. The coefficient of determination obtained from the plots of the five pseudorotaxanes is high ($R^2 = 0.95$). This indicates that resonance effect of the aromatic group A is significant among the mono-substituted aromatic groups. These results indicate that the pseudorotaxanes bearing mono- and disubstituted aromatic group A showed that the electronic nature of A influenced the relative positions and orientations of the aryl groups A and B.

The centroid distance ($d$) and dihedral angle ($\theta$) of 1i-Ni (3.665 Å and 4.59°) were smaller than those of 1i with PF$_6$ anion (3.710 Å and 6.20°). Such effects of the counter anion on the structure of cationic pseudorotaxane are ascribed to the different co-conformation of the pseudorotaxanes caused by the counter anions (vide supra) [50].

Theoretical studies compared three possible geometries for the aromatic interactions, slipped-parallel, parallel, and perpendicular ones (Scheme 2). Tsuzuki et al. calculated stabilities of the benzene dimers as the function of distance ($d$) and angles ($\theta$) between them and reported the optimized position for slipped paralleled conformation ($d = 3.5$ Å, $\Delta G^\circ = -2.48$ kcal mol$^{-1}$ (at the CCSD(T) level)) which is more stable than the parallel type interaction ($\Delta G^\circ = -1.48$ kJ mol$^{-1}$) and similar to C-H···π interaction ($\Delta G^\circ = -2.46$ kJ mol$^{-1}$) [59–62]. Thus, the energy differences among the possible interacted structures are small. Recently, parallel stacking of the aromatic rings (Scheme 2b) was found in the crystals of polyhedral oligomeric silsesquioxane (POSS) derivatives, although it was considered to be less stable than the others [63]. The combination of two aromatic rings at close positions was known to influence stability of their π-π stacking. As a further important factor, donor–acceptor interaction was known to stabilize the aromatic interaction significantly.

![Scheme 2. Typical geometries of benzene dimers, (a) slipped-parallel, (b) parallel, and (c) perpendicular.](image)

Figure 4 depicts partial X-ray dimer structures of 1a and 1j, showing the relative positions of their A and B rings. Both A and B rings of 1a and 1j show slipped-parallel type stacking (Scheme 2a). The overlapping of π electrons between A and B rings of 1a looks larger than that of 1j. The $d$ and $\theta$ values of 1a (3.553 Å and 3.65°) and of 1j (3.779 Å and 7.94°) indicate that the C$_6$H$_3$-3,4-Cl$_2$ ring of 1a and the catechol ring of DB24C8 is closer and less tilted than those of the C$_6$H$_3$-4-OMe ring of 1i and the catechol ring of DB24C8 because of stronger donor–acceptor interaction in the former system.

Stoddart, Williams, and their co-workers investigated a full series of pseudorotaxanes composed of DB24C8 and bis(aryl methyl) ammonium in the solid state and in solution. They observed a clear relationship between the stability constants for the pseudorotaxane and the electron donating ability of the substituents of the aryl groups of the axle components in CDCl$_3$ and CD$_3$CN·CDCl$_3$ [55]. Higher stability of pseudorotaxanes possessing aryl groups with electron-withdrawing groups, such as NO$_2$ and COOH groups, at the para position can be attributed to the aromatic interaction between the axle and macrocyclic components. Although direct estimation of the aromatic interaction was difficult in the solutions, the results in the solid of this study state are related to the relative stability of the pseudorotaxanes in the solution.
Figure 4. Partial structures of pseudorotaxanes (a) 1a (left) and (b) 1j (right). Two close aromatic rings by crystallographic results and their schematic diagram are shown.

3. Materials and Methods

3.1. General

$^1$H NMR spectra were acquired on a MERCURY300 (Varian, Tokyo, Japan), EX-400 (JEOL, Tokyo, Japan) and a AV-400M (Bruker, Yokohama, Japan). The chemical shifts were referenced with respect to CHCl$_3$ (δ 7.26), CD$_2$HCN (δ 1.93) for $^1$H, and CDCl$_3$ (δ 77.0), CD$_3$CN (δ 1.30) for $^{13}$C as internal standards. Elemental analysis was carried out with a CHNS-932 (LECO, Tokyo, Japan) or MT-5 CHN (Yanaco, Tokyo, Japan) autorecorder. FTIR spectra were measured with a FTIR-8100A (Shimadzu, Kyoto, Japan) and FT/IR-4100 (JASCO, Tokyo, Japan). H$_2$NCH$_2$Ar (Ar = -C$_6$H$_4$-4-Br, -C$_6$H$_3$-3-F-4-Me) was prepared by reaction of LiAlH$_4$ and NCAr in THF under reflux condition. Other chemicals are commercially available and used without further purification.

3.2. Crystal Synthesis of [(FcCH$_2$NH$_2$CH$_2$C$_6$H$_3$-3,4-Cl$_2$)(DB24C8)]PF$_6$ (1a)

Yellow crystals of pseudorotaxane 1a were obtained by slow evaporation of CH$_2$Cl$_2$/Et$_2$O solution of 2a (52 mg, 0.10 mmol) and DB24C8 (46 mg, 0.10 mmol). 1a was obtained with 10% yield. Synthesis details and spectroscopic results of the precursors of pseudorotaxanes and cif files are in Supplementary Materials.

Elemental analysis: calcd (%) for C$_{42}$H$_{50}$NO$_8$FeF$_6$Cl$_2$: C, 52.08; H, 5.20; N, 1.45; Cl, 7.32; found: C, 51.58; H, 4.93; N, 1.45; Cl, 7.38.

3.3. Crystal Synthesis of [(FcCH$_2$NH$_2$CH$_2$C$_6$H$_3$-3,4-F$_2$)(DB24C8)]PF$_6$ (1b)

Yellow crystals of pseudorotaxane 1b were obtained by slow evaporation of acetone/hexane solution of 2b (46 mg, 0.093 mmol) and DB24C8 (49 mg, 0.11 mmol). 1b was obtained with 57% yield.

Elemental analysis: calcd (%) for C$_{42}$H$_{50}$NO$_8$FeF$_8$: C, 53.91; H, 5.39; N, 1.50; found: C, 53.81; H, 5.39; N, 1.52.

3.4. Crystal Synthesis of [(FcCH$_2$NH$_2$CH$_2$C$_6$H$_4$-4-F)(DB24C8)]PF$_6$ (1c)

Yellow crystals of pseudorotaxane 1c were obtained by slow evaporation of acetone/hexane solution of 2c (47 mg, 0.10 mmol) and DB24C8 (44 mg, 0.099 mmol). 1c was obtained with 49% yield.
Elemental analysis: calcd (%) for C_{42}H_{51}NO_{8}FeF_{7}P: C, 54.97; H, 5.60; N, 1.53; found: C, 54.92; H, 5.65; N, 1.89.

3.5. Crystal Synthesis of [(FcCH_{2}NH_{2}CH_{2}C_{6}H_{4}-4-Cl)(DB24C8)]PF_{6} (1d)

Yellow crystals of pseudorotaxane 1d were obtained by slow evaporation of acetone/hexane solution of 2d (48 mg, 0.10 mmol) and DB24C8 (45 mg, 0.10 mmol). 1d was obtained with 74% yield.

Elemental analysis: calcd (%) for C_{42}H_{51}NCIF_{6}FeO_{8}P: C, 54.00; H, 5.50; N, 1.50; found: C, 53.69; H, 5.45; N, 1.48.

3.6. Crystal Synthesis of [(FcCH_{2}NH_{2}CH_{2}C_{6}H_{4}-4-Br)(DB24C8)]PF_{6} (1e)

Yellow crystals of pseudorotaxane 1e were obtained by slow evaporation of CHCl_{3}/acetone (2.0 mL/0.5 mL) solution of 2e (53 mg, 0.10 mmol) and DB24C8 (45 mg, 0.10 mmol). 1e was obtained with 85% yield.

Elemental analysis: calcd (%) for C_{42}H_{51}NBrF_{6}FeO_{8}P(H_{2}O)_{0.5}: C, 51.08; H, 5.31; N, 1.42; found: C, 50.99; H, 5.35; N, 1.45.

3.7. Crystal Synthesis of [(FcCH_{2}NH_{2}CH_{2}C_{6}H_{3}-3-F-4-Me)(DB24C8)]PF_{6} (1f)

Yellow crystals of pseudorotaxane 1f were obtained by slow evaporation of CH_{2}Cl_{2}/Et_{2}O solution of 2f (47 mg, 0.094 mmol) and DB24C8 (45 mg, 0.10 mmol). 1f was obtained with 41% yield.

Elemental analysis: calcd (%) for C_{43}H_{53}NF_{7}FeNO_{8}P: C, 55.43; H, 5.73; N, 1.50; found: C, 55.45; H, 5.29; N, 1.55.

3.8. Crystal Synthesis of [(FcCH_{2}NH_{2}CH_{2}C_{6}H_{4}-4-I)(DB24C8)]PF_{6} (1g)

Yellow crystals of pseudorotaxane 1g were obtained by slow evaporation of CH_{2}Cl_{2}/Et_{2}O solution of 2g (57 mg, 0.10 mmol) and DB24C8 (45 mg, 0.10 mmol). 1g was obtained with 69% yield.

Elemental analysis: calcd (%) for C_{42}H_{51}NIF_{6}FeNO_{8}P: C, 49.19; H, 5.01; N, 1.37; found: C, 49.29; H, 4.98; N, 1.37.

3.9. Crystal Synthesis of [(FcCH_{2}NH_{2}CH_{2}C_{6}H_{4}-4-Me)(DB24C8)][Ni(dmit)_{2}] (1i-Ni)

Compound [FeC_{6}H_{5}NH_{2}CH_{2}C_{6}H_{4}-4-Me][Ni(dmit)_{2}] (2i-Ni) was obtained by anion exchange of [FeC_{6}H_{5}NH_{2}CH_{2}C_{6}H_{4}-4-Me][PF_{6}] with Li[Ni(dmit)_{2}]. Black crystals of pseudorotaxane 1i-Ni were obtained by slow evaporation of CH_{2}Cl_{2}/Et_{2}O solution of 2i-Ni (77 mg, 0.10 mmol) and DB24C8 (45 mg, 0.10 mmol) with 43% yield. The crystals revealed the molecular structure but did not provide satisfactory analytical results.

3.10. X-ray Crystallography

Data were collected on a Rigaku Saturn CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å). All H atoms were fixed at ideal positions. CCDC 1032569-1032577 and 2122024 contain the supplementary crystallographic data for complex 1a-1g, and 1i-Ni. Table 2 summarizes the structural data used in Figure 3a,b.

4. Conclusions

The pseudorotaxanes of DB24C8 and ferrocenylmethyl(arylmethyl)ammonium in this study were stabilized by three-point support in the crystals, N-H···O hydrogen bonds, C(Cp)–H···π interaction between the ferrocenyl group and a catechol group, and aromatic interaction between the aryl group of the axle component and a catechol group. Choice of the third interaction, either π···π interaction (α-form) or C-H···π interaction (β-form), was reported to depend on the counter anions, as shown for 2i in our previous papers [46,47,50]. Crystals in α-form and those in β-form exhibit different IR peak positions and N···O distance, relating to the hydrogen bonds between the axle and macrocyclic molecules, as shown in Table 1. This study revealed that the aryl group of the axle molecules...
influenced structural parameters around the two aromatic groups with a π···π interaction. The aryl group with electron-withdrawing substituents enhanced the aromatic interaction and stabilized the pseudorotaxane. Findings in this study deepened full understanding of structures of the pseudorotaxanes with a ferrocenyl group.

**Supplementary Materials:** The following supporting information can be downloaded online, synthesis details and spectroscopic results of the precursors of pseudorotaxanes and cif files of 1b–1g and 1i-Ni.

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