Kinetic and Spectroscopic Studies on α-Cyclodextrin Rotaxanes with Pentacyano(cyanopyridinium)ferrate(II) Stoppers

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[2]Pseudorotaxanes have been prepared by threading linear chains of the type $[R(CH_2)_nR]^{2+}$ (where R = 3- or 4-cyanopyridine and $n = 9$ or 10) through α-cyclodextrin (α-CD), and subsequently converted to the corresponding [2]rotaxane species by coordinating bulky $[Fe(CN)_5]^{3-}$ end groups. The lability of the iron(II)-cyanopyridinium bonds also permits the spontaneous rotaxane self-assembly upon cyclodextrin addition to the iron dimer complexes. The mechanism for this process involves the rate-determining dissociation of a $[Fe(CN)_5]^{3-}$ unit ($(7 \pm 1) \times 10^{-2}$ s^{-1} at 25 °C for $[(NC)_5Fe(4CNpyr(CH_2)_94CNpyr)Fe(CN)_5]^{4-}$). The stability constants for the α- and β-CD inclusion complexes; $\{AD\text{-}CNpyr{\cdot}CD\}^+$ and $[Fe(CN)_5\{AD\text{-}CNpyr{\cdot}CD\}]^{2-}$ (AD-$CNpyr^+$ = 1-adamantan-1′-yl-3- and -4-cyanopyridinium), have been determined by ^1H NMR spectroscopy and ligand substitution kinetic studies. The rate constants for the ligand substitution reactions of the $[Fe(CN)_5(AD\text{-}CNpyr)]^{2-}$ and $[Fe(CN)_5(CNpyr(CH_2)_nCNpyr)]^-$ complexes exhibited significant diminutions in the presence of α- and β-CD, owing to inclusions of the free and coordinated cationic ligands.

Introduction

Rotaxanes are supramolecular species comprising a cyclic molecular bead which is threaded by a linear chain and stoppered by bulky end units, thus preventing the complex from dissociating into its cyclic and linear molecular components.[1−4] Among the cyclic components which have been employed in the synthesis of rotaxanes, the cyclodextrins, a series of cyclic oligosaccharides normally consisting of six (α-CD), seven (β-CD), or eight (γ-CD) α-(1→4)-linked D-(+)-glucopyranose units, have been the subject of considerable investigations.[5−18] [2]Rotaxanes stoppered by transition metal complexes have generally been prepared by reacting a semirotaxane (bearing one bulky end unit) with a second metal complex or organic end unit.[8,9,11,14−18] We recently reported the results of kinetic and spectroscopic investigations of the mechanism of the formation of a series of stable α-cyclodextrin rotaxanes of the type $[(NC)_5Fe\{R(CH_2)_nR'{\cdot}\alpha\text{-}CD\}Fe(CN)_5]^{4-}$, with symmetric and asymmetric threads where R and R′ = pyrazine and/or 4,4′-bipyridine, with $n = 8-12$.[14−16] These [2]rotaxanes will self-asssemble irrespective of the order of the addition of the α-CD, $[R(CH_2)_nR']^{2+}$ ligand, and $[Fe(CN)_5]^{3-}$ components. The slower route involves initial formation of an iron dimer complex, $[(NC)_5Fe(R(CH_2)_nR')Fe(CN)_5]^{4-}$, which will not permit direct threading through α-CD because of the bulky pentacyanoferrate(II) stoppers. Slow dissociation of a $[Fe(CN)_5]^{3-}$ unit, however, followed by the α-CD inclusion of the coordinated bridging ligand yields a semirotaxane, which may be rapidly recomplexed by $[Fe(CN)_5OH_2]^{3-}$. The rate constants for this self-assembly process are dependent on the lability of the iron−nitrogen bond.

In the present study we have investigated the use of dicationic bridging ligands where R = 3- and 4-cyanopyridine, which yield complexes with more labile Fe−N (nitrile) bonds than for corresponding complexes with either pyrazine or 4,4′-bipyridine. The stability constants for the [2]pseudorotaxanes $\{CNpyr(CH_2)_nCNpyr{\cdot}\alpha\text{-}CD\}^{2+}$ (CNpyr = 3-cyanopyridine ($n = 10$), 4-cyanopyridine ($n = 9$, 10)) have been determined by means of ^1H NMR spectroscopic titrations. The kinetics and mechanism of the self-assembly of the $[(NC)_5Fe\{4CNpyr(CH_2)_9 4CNpyr{\cdot}\alpha\text{-}CD\}Fe(CN)_5]^{4-}$ rotaxane from the dimer have been studied using stopped-flow spectrophotometric techniques. In addition, we report the results of kinetic and spectroscopic studies on the ligand substitution reactions involving α- and

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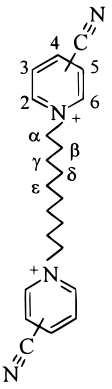
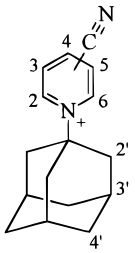


[CNpyr(CH$_2$)$_{10}$CNpyr]$^{2+}$



[ADCNpyr]$^+$

β-cyclodextrin inclusion complexes of the $[Fe(CN)_5(MeCNpyr)]^{2-}$ ([MeCNpyr]$^+$ = 1-methyl-3- and -4-cyanopyridinium), $[Fe(CN)_5(AD\text{-}CNpyr)]^{2-}$ (AD-CNpyr$^+$ = 1-adamantan-1′-yl-3- and -4-cyanopyridinium), $[Fe(CN)_5(CNpyr(CH_2)_nCNpyr)]^-$, and $[(NC)_5Fe(CNpyr(CH_2)_nCNpyr)Fe(CN)_5]^{4-}$ ions. The host−guest behaviors of these complexes are compared with the results of previous studies on similar pentacyanoferrate(II) complexes containing neutral and cationic N-heterocyclic ligands.[19,20]

Experimental Section

Materials. The α- and β-cyclodextrins (Aldrich) were dried at 80 °C under reduced pressure for at least 12 h prior to use. 4-Cyanopyridine, 3-cyanopyridine, 1,9-dibromononane, 1,10-diiododecane, 1-bromoadamantane, and iodomethane (Aldrich) were used as received. Sodium amminepentacyanoferrate(II) hydrate, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, was prepared by a literature method[21] and recrystallized from concentrated ammonia/methanol solution. The $[Fe(CN)_5OH_2]^{3-}$ ion was generated in solution, by the rapid aquation of the ammine salt, at low concentrations ($<10^{-4}$ M) to minimize dimerization processes.[22]

1-Adamantan-1′-yl-3- and -4-cyanopyridinium Perchlorates. [AD3CNpyr]ClO_4 and [AD4CNpyr]ClO_4 were prepared according to the method of Katritzky *et al.*[23] as modified by Macartney and Shortreed.[19] The product was recrystallized from water to yield white needles.

[AD3CNpyr]$ClO_4\cdot H_2O$. Mp: 251 °C. Anal. Calcd for $C_{16}H_{19}N_2ClO_4\cdot H_2O$: C, 53.86; H, 5.93; N, 7.85. Found: C, 54.39; H, 5.80; N, 8.35 (Canadian Microanalytical Services, Delta, BC). ^{1}H NMR (D_2O): δ 9.72 (s, 1H, H_2), 9.46 (dd, 1H, H_6, $J_{5,6}$ = 5.1, $J_{4,6}$ = 1.3 Hz), 9.07 (dt, 1H, H_4, $J_{4,5}$ = 8.1 Hz), 8.31 (dd, 1H, H_5), 2.40 (m, 3H, $H_{3'}$), 2.36 (d, 6H, $H_{2'}$, $J_{2',3'}$ = <0.5 Hz), 1.85 (d, 3H, $H_{4a'}$), 1.82 (d, 3H, $H_{4b'}$, $J_{4a',4b'}$ = 12.6 Hz) ppm. ^{13}C NMR (D_2O): δ 155.0 (C_6), 154.3 (C_4), 143.4 (C_2), 126.7 (C_5), 118.1 (C_3), 112.3 ($C_{C\equiv N}$), 43.8 ($C_{2'}$), 36.6 ($C_{4'}$), 32.3 ($C_{3'}$) ppm.

[AD4CNpyr]$ClO_4\cdot H_2O$. Mp: 219 °C. Anal. Calcd for $C_{16}H_{19}N_2ClO_4\cdot H_2O$: C, 53.86; H, 5.93; N, 7.85. Found: C, 54.26; H, 5.62; N, 7.99. ^{1}H NMR (D_2O): δ 9.39 (d, 2H, H_2, $J_{2,3}$ = 7.2 Hz), 8.42 (d, 2H, H_3), 2.40 (m, 3H, $H_{3'}$), 2.35 (d, 6H, $H_{2'}$, $J_{2',3'}$ = <0.5 Hz), 1.84 (d, 3H, $H_{4a'}$), 1.80 (d, 3H, $H_{4b'}$, $J_{4a',4b'}$ = 12.6 Hz) ppm. ^{13}C NMR (D_2O): δ 129.0 (C_3), 112.5 ($C_{C\equiv N}$), 39.8 ($C_{2'}$), 32.5 ($C_{4'}$), 28.1 ($C_{3'}$) ppm.

1-Methyl-3-cyanopyridinium Iodide. [Me3CNpyr]I was prepared by a reported procedure[24] and recrystallized from ethanol to give yellow needles. Mp: 176−179 °C. Anal. Calcd for $C_7H_7N_2I$: C, 34.17; H, 2.87; N, 11.39. Found: C, 34.39; H, 2.98; N, 11.26. ^{1}H NMR (D_2O): δ 9.49 (s, 1H, H_2), 9.11 (d, 1H, H_6, $J_{5,6}$ = 6.2 Hz), 8.94 (d, 1H, H_4, $J_{4,5}$ = 8.2 Hz), 8.26 (dd, 1H, H_5), 4.48 (s, 3H, H_{Me}) ppm.

1-Methyl-4-cyanopyridinium Iodide. [Me4CNpyr]I was prepared by stirring a mixture of 4-cyanopyridine (1.0 g) and methyl iodide (7 g) in 12 mL of DMF for 12 h at 50 °C. The product was precipitated by adding 100 mL of diethyl ether to the cooled reaction solution, and brown crystals were obtained upon recrystallization from ethanol. Mp: 169−170 °C. Anal. Calcd for $C_7H_7N_2I$: C, 34.17; H, 2.87; N, 11.39. Found: C, 34.41; H, 2.97; N, 11.36. ^{1}H NMR (D_2O): δ 9.13 (d, 2H, H_2, $J_{2,3}$ = 6.9), 8.51 (d, 2H, H_3) ppm. ^{1}H NMR (DMSO-d_6): δ 4.40 (s, 3H, H_{Me}) ppm.

1,1′-(1,10-Decanediyl)bis(cyanopyridinium) Diiodide and 1,1′-(1,9-Nonanediyl)bis(4-cyanopyridinium) Diiodide. The compounds [3CNpyr$(CH_2)_{10}$3CNpyr]I_2, [4CNpyr$(CH_2)_{10}$4CNpyr]I_2, and [4CNpyr-$(CH_2)_9$4CNpyr]I_2 were prepared by modifications of the method of Attalla *et al.*[25] as described previously.[16]

[3CNpyr(CH$_2$)$_{10}$3CNpyr]I$_2$. Mp: 165−167 °C. Anal. Calcd for $C_{22}H_{28}N_4I_2$: C, 43.87; H, 4.69; N, 9.30. Found: C, 44.00; H, 4.71; N, 9.12. ^{1}H NMR (D_2O): δ 9.51 (s, 2H, H_2), 9.17 (d, 2H, H_6, $J_{6,5}$ = 6.1 Hz), 8.95 (d, 2H, H_4, $J_{4,5}$ = 8.1 Hz), 8.29 (dd, 2H, H_5), 4.71 (t, H_4, H_α, $J_{\alpha,\beta}$ = 7.4 Hz), 2.04 (br m, 4H, H_β), 1.35−1.28 (m, 12H, $H_{\gamma-\epsilon}$) ppm. ^{13}C NMR (D_2O): δ 148.7 (C_4), 148.0 (C_2,C_6), 129.0 (C_5), 114.1 and 113.3 (C_3, $C_{C\equiv N}$), 63.1 (C_α), 30.4 (C_β), 28.3 (C_ϵ), 28.0(C_δ), 25.1 (C_γ) ppm.

[4CNpyr(CH$_2$)$_{10}$4CNpyr]I$_2$. Mp: 198−200 °C. Anal. Calcd for $C_{22}H_{28}N_4I_2$: C, 43.87; H, 4.69; N, 9.30. Found: C, 43.86; H, 4.84; N, 9.05. ^{1}H NMR (D_2O): δ 9.11 (d, 4H, H_2, $J_{2,3}$ = 6.6 Hz), 8.45 (d, 4H, H_3), 2.01 (br m, 4H, H_β), 1.31−1.23 (m, 12H, $H_{\gamma-\epsilon}$) ppm. ^{13}C NMR (D_2O): δ 145.9 (C_2), 131.3 (C_3), 128.1 (C_4), 114.3 (C_5), 63.3 (C_α), 30.6 (C_β), 28.3 (C_ϵ), 28.0 (C_δ), 25.2 (C_γ) ppm.

[4CNpyr(CH$_2$)$_9$4CNpyr]I$_2$. Mp: 181−183 °C. Anal. Calcd for $C_{21}H_{26}N_4I_2$: C, 42.88; H, 4.45; N, 9.52. Found: C, 43.13; H, 4.48; N, 9.51. ^{1}H NMR (D_2O): δ 9.15 (d, 4H, H_2, $J_{2,3}$ = 6.6 Hz), 8.49 (d, 4H, H_3), 2.05 (br m, 4H, H_β), 1.35 (m, 10H, $H_{\gamma-\epsilon}$) ppm.

Physical Measurements. The kinetics of the ligand substitution reactions of the substituted pentacyanoferrate(II) complexes, $[Fe(CN)_5L]^{(3-n)-}$, were determined by stopped-flow (Applied Photophysics SX-17MV) or conventional (Hewlett-Packard 8452A) mixing techniques. The reactions were generally carried out under pseudo-first-order conditions of excess entering ligand concentrations. Plots of $\ln(A_t - A_\infty)$ or $\ln(A_\infty - A_t)$ against time were linear for at least 3 half-lives, with six to eight replicate experiments performed for the stopped-flow measurements and one experiment for the ligand dissociation reactions. In the studies of the formation of the iron dimer complexes, pseudo-first-order excesses of freshly prepared $[Fe(CN)_5OH_2]^{3-}$ ion solutions were employed, and the kinetic traces were fit to two consecutive first-order reactions using the Applied Photophysics software. The reaction temperature was maintained to within 0.1 °C over the range 5−32 °C by means of external circulating water baths. The ionic strength was kept at 0.10 M by using sodium chloride.

The ^{1}H NMR spectra were recorded on Bruker AC-200 and AM-400 instruments in D_2O, utilizing the residual solvent proton signal as the reference. The mass spectrometry measurements were obtained on a VG Quattro quadrupole mass spectrometer, with an atmospheric pressure electrospray source. Samples, as solutions in distilled water with α-cyclodextrin, were introduced into the source at a flow rate of 5 mL min^{-1}.

The stability constants for the α- and β-cyclodextrin inclusion complexes of the [AD-CNpyr]$^+$ ligands and the α-CD pseudorotaxanes of the [4CNpyr$(CH_2)_9$4CNpyr]$^{2+}$ and [CNpyr$(CH_2)_{10}$CNpyr]$^{2+}$ ligands were determined from ligand substitution kinetic data and ^{1}H NMR titrations by the application of nonlinear least-squares and Simplex optimization programs to the equations for a 1:1 guest-host model, as described previously.[16,20]

Results and Discussion

Guest−Host Inclusion Complexes. The stability constants, K_L, for the inclusion complexes formed between the 1-adaman-

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Table 1. Limiting ^{1}H NMR Chemical Shift Changes ($\Delta\delta_{lim}$) and Inclusion Stability Constants for the [AD-CNpyr]$^+$ Ligands and [Fe(CN)$_5$(AD-CNpyr)]$^{2-}$ Complexes with α- and β-Cyclodextrins[a]

	$\Delta\delta_{lim}$ (ppm)							
	[AD3CNpyr]$^+$		[Fe(CN)$_5$(AD3CNpyr)]$^{2-}$		[AD4CNpyr]$^+$		[Fe(CN)$_5$(AD4CNpyr)]$^{2-}$	
proton	α-CD	β-CD	α-CD	β-CD	α-CD	β-CD	α-CD	β-CD
$H_{2'}$	+0.08	+0.11	+0.11	+0.10	+0.09	+0.12	+0.11	+0.12
$H_{3'}$	+0.13	+0.16	+0.16	+0.15	+0.14	+0.20	+0.17	+0.20
$H_{4'}$	+0.10	+0.10	+0.12	+0.10	+0.09	+0.11	+0.11	+0.11
H_2	−0.03	−0.04	−0.03		−0.01	−0.01	+0.01	−0.02
H_3					+0.03	+0.09	+0.06	+0.09
H_4	−0.01	+0.07	+0.01	+0.09				
H_5	−0.01	+0.08	+0.01	+0.08				
H_6	−0.01	−0.02	+0.04	−0.05				
K_L (M^{-1})	150 ± 30	1800 ± 300			103 ± 25	3260 ± 800		
K_{ML} (M^{-1})			60 ± 10	1850 ± 400			95 ± 15	3570 ± 250

[a] In D_2O at 25 °C, I = 0.10 M (NaCl).

tan-1′-ylcyanopyridinium cations and the α- and β-cyclodextrins (eq 1) were determined at 25 °C by means of ^{1}H NMR chemical shift titrations in D_2O (I = 0.10 M (NaCl)).

$$[\text{AD-CNpyr}]^+ + \text{CD} \overset{K_L}{\rightleftharpoons} \{\text{AD-CNpyr}\cdot\text{CD}\}^+ \qquad (1)$$

The formations of the inclusion complexes of α- and β-CD with the [AD-CNpyr]$^+$ ligands result in changes in the chemical shifts ($\Delta\delta_{obs}$) for the adamantyl and pyridinium proton resonances, with respect to their positions for the free ligand (eq 2). Using the changes in the chemical shifts ($\Delta\delta_{obs}$) of the

$$\Delta\delta_{obs} = \frac{\Delta\delta_{lim}[\{\text{AD-CNpyr}\cdot\text{CD}\}^+]}{[\text{AD-CNpyr}^+]_T} \qquad (2)$$

adamantyl and pyridinium protons, the inclusion stability constants (K_L) and the limiting chemical shift changes ($\Delta\delta_{lim}$) for {AD3CNpyr·CD}$^+$ and {AD4CNpyr·CD}$^+$ with α- and β-CD were determined at 25 °C at I = 0.10 M (NaCl) and are presented in Table 1.[16,20] The values of $\Delta\delta_{lim}$ are generally similar in sign and magnitude to those reported for the adamantan-1-ylammonium[26] and the adamantan-1-ylpyrazinium[19] cations, which exhibit similar inclusion stability constants.

The larger stability constants determined for the [AD-CNpyr]$^+$ ligands with β-CD are due primarily to the complementarity of the fit of the adamantane ring (approximately 7 Å diameter) in the β-CD cavity. With the smaller cavity of α-CD, the adamantyl portion of the [AD-CNpyr]$^+$ ligands cannot be included as deeply as in the case of β-CD, and therefore smaller stability constants are observed. When the adamantyl group is replaced by the much smaller methyl group, no significant inclusion of the [MeCNpyr]$^+$ ligands in the cyclodextrin cavities is observed, as demonstrated by the lack of change ($\Delta\delta_{lim}$ < 5 Hz) in the chemical shifts of the [MeCNpyr]$^+$ ligand proton resonances upon addition of either α- or β-CD.

The inclusion stability constants determined for the [AD-CNpyr]$^+$ guests with both α- and β-CD are comparable to those for the [ADpyz]$^+$ ligand (pyz = pyrazinium),[19] which is similar in size and charge. The lack of significant differences in the guest-host properties of the [AD3CNpyr]$^+$, [AD4CNpyr]$^+$, and [ADpyz]$^+$ ligands strongly favor a model in which the hydrophobic adamantyl group rather than the more hydrophilic N-heterocyclic ring occupies the cyclodextrin cavity. Other substituted adamantanes (such as ADCOOH, ADCOO$^-$, AD-NH$_2$, ADNH$_3^+$),[27] which are able to hydrogen-bond with the cyclodextrin hydroxyl groups upon inclusion, display binding constants that are significantly larger (10^4−10^5 M^{-1}) than those obtained for the [AD-CNpyr]$^+$ ligands.

[2]Pseudorotaxane Complexes. The additions of α-cyclodextrin to aqueous solutions of the dicationic [3CNpyr(CH$_2$)$_{10}$-3CNpyr]$^{2+}$ and [4CNpyr(CH$_2$)$_{10}$4CNpyr]$^{2+}$ ligands result in the formation of [2]pseudorotaxane complexes (eq 3). The presence

$$[\text{CNpyr(CH}_2)_{10}\text{CNpyr}]^{2+} + \alpha\text{-CD} \overset{K_L}{\rightleftharpoons} \{\text{CNpyr(CH}_2)_{10}\text{CNpyr}\cdot\alpha\text{-CD}\}^{2+} \qquad (3)$$

of the [2]pseudorotaxanes, {L·α-CD}$^{2+}$, in aqueous solutions of the [CNpyr(CH$_2$)$_{10}$CNpyr]$^{2+}$ ligands with excess α-CD, was detected by electrospray mass spectroscopy (ES-MS). In the ES-MS spectra, signals were observed at m/z = 660.4 for {L·α-CD}$^{2+}$ (expected at m/z = 660.3) and 669.4 for {L·α-CD·H$_2$O}$^{2+}$, for both complexes.

The stability constants for the [2]pseudorotaxanes, formed by the addition of α-CD to the [CNpyr(CH$_2$)$_{10}$CNpyr]$^{2+}$ ligands, were determined by ^{1}H NMR titrations. The splittings of the aromatic and aliphatic proton resonances of the threading ligand (Figure 1), arising from the asymmetry of the cyclodextrin cavity, are indicative of slow pseudorotaxane assembly processes on the ^{1}H NMR time scale.[14−16] The cyclodextrin inclusion stability constants (K_L) were determined, by means of ^{1}H NMR titrations of the ligand with α-CD in D_2O (I = 0.10 M (NaCl)), to be 610 ± 130 and 900 ± 230 M^{-1} at 25 °C for the {3CNpyr(CH$_2$)$_{10}$3CNpyr·α-CD}$^{2+}$ and {4CNpyr(CH$_2$)$_{10}$4CN-pyr·α-CD}$^{2+}$ complexes, respectively. The cyclodextrin stability constants measured previously for related ligands are of similar magnitude: 1400 ± 130 M^{-1} for {pyz(CH$_2$)$_{10}$pyz·α-CD}$^{2+}$,[16] 1500 ± 100 M^{-1} for {bpy(CH$_2$)$_{10}$bpy·α-CD}$^{2+}$,[20] and 1300 M^{-1} for {pyr(CH$_2$)$_{10}$pyr·α-CD}$^{2+}$.[6b]

The thermodynamic parameters associated with the stability constant for the {4CNpyr(CH$_2$)$_{10}$4CNpyr·α-CD}$^{2+}$ [2]pseudorotaxane were determined from a variable temperature (9−35 °C) ^{1}H NMR study. The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of reaction were calculated to be −12 ± 5 kJ mol^{-1} and +15 ± 14 J K^{-1} mol^{-1}, respectively. When D_2O solutions of {3CN-pyr(CH$_2$)$_{10}$3CNpyr·α-CD}$^{2+}$ and {4CNpyr(CH$_2$)$_{10}$4CNpyr·α-CD}$^{2+}$ pseudorotaxanes were heated up to 90 °C, no coalescences were observed in the split guest proton resonances. Coalescence was also not observed for the {pyz(CH$_2$)$_{10}$pyz·α-CD}$^{2+}$ pseudorotaxane up to 90 °C.[16] In the cases of the {bpy(CH$_2$)$_{10}$bpy·α-CD}$^{2+}$,[15] {pyr(CH$_2$)$_{10}$pyr·α-CD}$^{2+}$,[6b] and

(26) Selvidge, L. A.; Eftink, M. R.; Bystrom, K.; Perlmutter, H. D.; Kristol, D. *J. Am. Chem. Soc.* **1989**, *111*, 6765.

(27) Gelb, R. I.; Schwartz, L. M.; Laufer, D. A. *J. Am. Chem. Soc., Perkin Trans. 2* **1984**, 15.

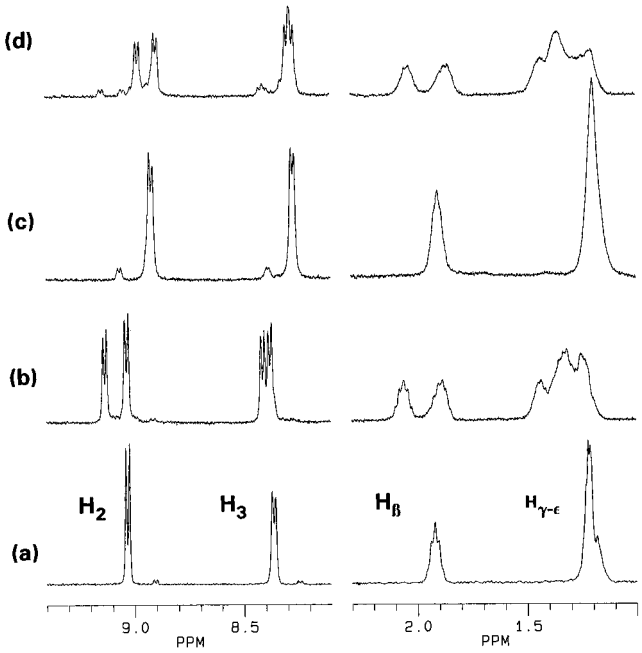

Figure 1. ^{1}H NMR spectra of (a) $[4CNpyr(CH_2)_94CNpyr]^{2+}$, (b) $\{4CNpyr(CH_2)_94CNpyr\cdot\alpha\text{-CD}\}^{2+}$, (c) $[Fe(CN)_5(4CNpyr(CH_2)_94CNpyr)]^-$, and (d) $[(NC)_5Fe\{4CNpyr(CH_2)_94CNpyr\cdot\alpha\text{-CD}\}Fe(CN)_5]^{4-}$ in D_2O.

$\{bpy(CH_2)_{10}pyz\cdot\alpha\text{-CD}\}^{2+}$ [16] pseudorotaxanes, however, coalescence of the H_β peaks, for example, yields one multiplet from the original two peaks, at approximately 75 °C. The lower coalescence temperatures for these pseudorotaxanes are indicative of faster dethreading processes, involving more facile desolvation of the pyridinium and 4,4′-bipyridinium head groups, which are less hydrophilic than the pyrazinium and the cyanopyridinium rings.

The kinetics of the dethreading (eq 4) of the $\{3CNpyr(CH_2)_{10}3CNpyr\cdot\alpha\text{-CD}\}^{2+}$ pseudorotaxane (3.3 mM) was investigated (using ^{1}H NMR spectroscopy), in the presence of an excess

$$\{3CNpyr(CH_2)_{10}3CNpyr\cdot\alpha\text{-CD}\}^{2+} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [3CNpyr(CH_2)_{10}3CNpyr]^{2+} + \alpha\text{-CD} \quad (4)$$

(12.1 mM) of a competing guest, $[bpy(CH_2)_{12}bpy]^{2+}$ (bpy = 4,4′-bipyridine). Rapid[28] and efficient capture of the released α-CD by the $[bpy(CH_2)_{12}bpy]^{2+}$ guest ($K_L = 3700 \pm 540$ M^{-1}) is expected (eq 5), such that the observed first-order rate constant

$$[bpy(CH_2)_{12}bpy]^{2+} + \alpha\text{-CD} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \{bpy(CH_2)_{12}bpy\cdot\alpha\text{-CD}\}^{2+} \quad (5)$$

corresponds to the rate-limiting dethreading of the $\{3CNpyr(CH_2)_{10}3CNpyr\cdot\alpha\text{-CD}\}^{2+}$ pseudorotaxane. At 25 °C, k_{-1} was determined to be $(2.7 \pm 0.3) \times 10^{-3}$ s^{-1}, with $\Delta H^{\ddagger} = 93 \pm 6$ kJ mol^{-1} and $\Delta S^{\ddagger} = 18 \pm 19$ J K^{-1} mol^{-1} calculated from measurements between 8 and 30 °C. From the stability constant $K_L = 900 \pm 230$ M^{-1}, and with $k_1 = k_{-1}K_L$, the rate constant, k_1, for the threading of α-CD by the $[3CNpyr(CH_2)_{10}3CNpyr]^{2+}$ dication(eq 4) was determined to be 2.4 ± 0.9 M^{-1} s^{-1}.

Pentacyanoferrate(II) Complexes. The ligand substitution reactions between the labile $[Fe(CN)_5OH_2]^{3-}$ ions and the cationic ligands (L^{n+}) in aqueous solution result in the rapid formation of $[Fe(CN)_5L]^{(3-n)-}$ complexes. The pentacyanoferrate(II) complexes with substituted 4-cyanopyridinium ligands exhibit metal-to-ligand charge transfer (MLCT) bands in the 545−560 nm range, while the λ_{max} values for the corresponding 3-cyanopyridinium complexes are observed between 445 and 460 nm. The addition of β-CD to a solution of the $[Fe(CN)_5(AD4CNpyr)]^{2-}$ complex produces a bathochromic shift in the MLCT band (Table 2), as observed previously for pentacyanoferrate(II) complexes containing $[ADpyz]^+$ [19] or several neutral 4-substituted pyridine ligands.[20]

The stability constants for the cyclodextrin inclusion complexes of the $[Fe(CN)_5(AD\text{-}CNpyr)]^{2-}$ ions, K_{ML}, were determined from ^{1}H NMR spectrometric titrations (eq 6), as above

$$[Fe(CN)_5(AD\text{-}CNpyr)]^{2-} + CD \overset{K_{ML}}{\rightleftharpoons} [Fe(CN)_5\{AD\text{-}CNpyr\cdot CD\}]^{2-} \quad (6)$$

for the free ligands (eq 5) and are presented, along with the $\Delta\delta_{lim}$ values, in Table 1.

Ligand Substitution Kinetics. The ligand substitution reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion with the cationic ligands in this study (eq 7) may be monitored by following the

$$[Fe(CN)_5OH_2]^{3-} + L^{n+} \xrightarrow{k_f^0} [Fe(CN)_5L]^{(3-n)-} + H_2O \quad (7)$$

appearance of the MLCT bands of the $[Fe(CN)_5L]^{(3-n)-}$ products (Tables 2 and 3). The observed pseudo-first-order rate constants display a first-order dependence on $[L^{n+}]$, and the second-order rate constants, k_f^0, determined at 25 °C and an ionic strength of 0.10 M (NaCl), are presented in Tables 2 and 3.

The rate constants for the formation of $[Fe(CN)_5L]^{(3-n)-}$, where $L^{n+} = [AD\text{-}CNpyr]^+$ and $[CNpyr(CH_2)_{10}CNpyr]^{2+}$, were observed to decrease as the concentrations of α- or β-cyclodextrin were increased (Figure 2). The second-order rate constants (k_f^{CD}) for the reactions of the included ligands (eq 8)

$$[Fe(CN)_5OH_2]^{3-} + \{L\cdot CD\}^{n+} \xrightarrow{k_f^{CD}} [Fe(CN)_5\{L\cdot CD\}]^{(3-n)-} \quad (8)$$

and the inclusion stability constants (K_L) were obtained from nonlinear least-squares fits of the experimental rate constants (k_f^{obs}) to eq 9.

$$k_f^{obs} = \frac{k_f^0 + k_f^{CD}K_L[CD]}{1 + K_L[CD]} \quad (9)$$

The values of k_f^0, k_f^{CD}, and K_L at 25 °C and the corresponding activation parameters are presented in Tables 2 and 3. There is reasonably good agreement in the magnitudes of the stability constants between the two methods of determination. The rate constants for the formation reactions of the $[Fe(CN)_5(MeCNpyr)]^{2-}$ complexes were determined to be 2500 ± 100 and 1850 ± 50 M^{-1} s^{-1} for the $[Me3CNpyr]^+$ and $[Me4CNpyr]^+$ ligands, respectively, and were not affected by the presence of α-CD (up to 20 mM) or β-CD (up to 15 mM). The independence of k_f^{obs} on [CD] supports the observation, by ^{1}H NMR, of a lack of significant ligand inclusion. This finding is

(28) The kinetics of the threading processes involving formation of the $\{3CNpyr(CH_2)_{10}3CNpyr\cdot\alpha\text{-CD}\}^{2+}$ and $\{4Phpyr(CH_2)_{10}4Phpyr\cdot\alpha\text{-CD}\}^{2+}$ (4Phpyr = 4-phenylpyridine) [2]pseudorotaxane complexes have also been investigated by using methyl orange as the competing guest (R. S. Wylie, personal communication). Threading rate constants of 1.6 and 4.6×10^4 M^{-1} s^{-1}, respectively were determined at 25.0 °C (I = 0.10 M (HCl/NaCl), pH 1.1). The rate constant for the threading of α-CD by the $bpy(CH_2)_{12}bpy^{2+}$ guest (k_2) might be expected to be somewhat slower than that for $4Phpyr(CH_2)_{10}4Phpyr^{2+}$, because of the more hydrophilic head groups, but would still be considerably faster than threading by the $3CNpyr(CH_2)_{10}3CNpyr^{2+}$ ligand (k_1).

Table 2. Parameters Associated with the Ligand Substitution Reactions of Pentacyanoferrate(II) Complexes with the $[AD3CNpyr]^+$, $[AD4CNpyr]^+$, and $[ADpyz]^+$ Ligands in the Presence of α- and β-Cyclodextrins[a]

parameter	ligand		
	$[AD3CNpyr]^+$	$[AD4CNpyr]^+$	$[ADpyz]^+$ [b]
λ_{max} (nm)	446	546	658
ϵ (M^{-1} cm^{-1})	5100	8200	14 000
λ^{CD}_{max} (nm)	446 (α)	546 (α)	672 (α)
	446 (β)	568 (β)	672 (β)
k_f^0 (M^{-1} s^{-1})	1680 ± 50	1340 ± 10	2520 ± 50
$\Delta H^{\ddagger}_f{}^0$ (kJ mol^{-1})	71 ± 1	73 ± 1	69 ± 2
$\Delta S^{\ddagger}_f{}^0$ (J K^{-1} mol^{-1})	54 ± 3	59 ± 3	51 ± 5
k_f^{CD}(M^{-1} s^{-1})	966 ± 25 (α)	825 ± 45 (α)	1110 ± 30 (α)
	811 ± 10 (β)	830 ± 25 (β)	905 ± 40 (β)
$\Delta H^{\ddagger}_f{}^{CD}$ (kJ mol^{-1})	71 ± 3(α)	79 ± 3 (α)	
	81 ± 1 (β)	81 ± 1 (β)	66 ± 2 (β)
$\Delta S^{\ddagger}_f{}^{CD}$ (J K^{-1} mol^{-1})	52 ± 8 (α)	75 ± 10 (α)	
	82 ± 3 (β)	81 ± 4 (β)	34 ± 7 (β)
K_L (M^{-1})	85 ± 5 (α)	70 ±2 (α)	165 ± 12 (α)
	2865 ± 200 (β)	3000 ± 500 (β)	3030 ± 250 (β)
$10^2 k_d$ (s^{-1})	7.7 ± 0.2	3.1 ± 0.1	0.0207 ± 0.0006
$\Delta H^{\ddagger}_d$ (kJ mol^{-1})	96 ± 7	89 ± 2	109 ± 1
$\Delta S^{\ddagger}_d$ (J K^{-1} mol^{-1})	55 ± 20	25 ± 7	52 ± 4
$10^2 k_d^{CD}$ (s^{-1})	5.0 ± 0.9 (α)	2.2 ± 0.4 (α)	0.0079 ± 0.0003 (α)
	4.5 ± 0.8 (β)	1.8 ± 0.3 (β)	0.0072 ± 0.0003 (β)
$\Delta H^{\ddagger}_d{}^{CD}$ (kJ mol^{-1})	100 ± 2 (α)	114 ± 3 (α)	
	90 ± 4 (β)	87 ± 3 (β)	119 ± 2 (β)
$\Delta S^{\ddagger}_d{}^{CD}$ (kJ mol^{-1})	67 ± 6 (α)	105 ± 8 (α)	
	33 ± 12 (β)	15 ± 9 (β)	74 ± 7 (β)
K_{ML} (M^{-1})	22 ± 3 (α)	55 ± 10 (α)	137 ± 7 (α)
	1240 ± 150 (β)	5600 ± 960 (β)	1850 ± 110 (β)

[a] Kinetic measurements at 25 °C, I = 0.10 M (NaCl); the (α) and (β) symbols refer to limiting parameters measured for α-CD and β-CD, respectively. [b] Reference 19.

Table 3. Parameters Associated with the Ligand Substitution Reactions of Pentacyanoferrate(II) Complexes with the $[3CNpyr(CH_2)_{10}3CNpyr]^{2+}$ and $[4CNpyr(CH_2)_{10}4CNpyr]^{2+}$ Ligands in the Presence of α-Cyclodextrin[a]

parameter	$[3CNpyr(CH_2)_{10}3CNpyr]^{2+}$	$[4CNpyr(CH_2)_{10}4CNpyr]^{2+}$
λ_{max}(ML) (nm)	456	552
ϵ(ML) (M^{-1} cm^{-1})	3200	5000
k_f^0 (M^{-1} s^{-1})	5200 ± 200	4200 ± 200
$\Delta H^{\ddagger}_f{}^0$ (kJ mol^{-1})	66 ± 4	72 ± 1
$\Delta S^{\ddagger}_f{}^0$ (J K^{-1} mol^{-1})	48 ± 10	65 ± 3
k_f^{CD} (M^{-1} s^{-1})	2260 ± 300	2160 ± 300
$\Delta H^{\ddagger}_f{}^{CD}$ (kJ mol^{-1})	68 ± 5	77 ± 1
$\Delta S^{\ddagger}_f{}^{CD}$ (J K^{-1} mol^{-1})	49 ± 15	78 ± 4
$k_{f2}{}^0$ (M^{-1} s^{-1})	1150 ± 36	870 ± 20
$k_{f2}{}^{CD}$ (M^{-1} s^{-1})	640 ± 50	500 ± 50
K_L (M^{-1})	810 ± 160	2020 ± 160
$10^2 k_d$ (s^{-1})	9.87 ± 0.25	3.81 ± 0.10
$\Delta H^{\ddagger}_d$ (kJ mol^{-1})	106 ± 2	89 ± 2
$\Delta S^{\ddagger}_d$ (J K^{-1} mol^{-1})	90 ± 6	27 ± 6
$10^2 k_d^{CD}$ (s^{-1})	4.68 ± 0.86	2.61 ± 0.48
$\Delta H^{\ddagger}_d{}^{CD}$ (kJ mol^{-1})	103 ± 3	89 ± 2
$\Delta S^{\ddagger}_d{}^{CD}$(J K^{-1} mol^{-1})	79 ± 8	23 ± 7
K_{ML} (M^{-1})	400 ± 50	850 ± 150

[a] Kinetic measurements at 25 °C, I = 0.10 M (NaCl).

consistent with a positioning of the α-cyclodextrin in the $\{CNpyr(CH_2)_{10}CNpyr\cdot\alpha\text{-}CD\}^{2+}$ pseudorotaxanes around the decamethylene chain, rather than over the cyanopyridinium head groups.

The ligand substitution reactions proceed by an ion pair dissociative (D_{IP}) mechanism,[22,29] and the rate constants and activation parameters for the reaction of the $[AD\text{-}CNpyr]^+$ ligands are in good agreement with those reported for other monocationic ligands, including $[ADpyz]^+$ (Table 2). The rate constants for the $[AD\text{-}CNpyr]^+$ ligands are lower than that for the $[ADpyz]^+$ ion due to the greater distance between the positive charge and the nitrogen donor atom. This proximity effect likely also explains the somewhat larger rate constants determined for the $[Me3CNpyr]^+$, $[AD3CNpyr]^+$, and $[3CNpyr(CH_2)_{10}3CNpyr]^{2+}$ ligands compared to the isomeric $[Me4CNpyr]^+$, $[AD4CNpyr]^+$, and $[4CNpyr(CH_2)_{10}4CNpyr]^{2+}$ ligands, respectively (Tables 2 and 3).

The decrease in the observed second-order rate constants upon cyclodextrin inclusion of the entering ligand (Figure 2, Tables 2 and 3), which has been observed with a variety of neutral[20] and cationic[16,19] N-heterocyclic ligands, may be related to a decrease in the proportion of "effective" ion pairs, those which lead to substitution by placing the donor atom of the ligand in close proximity to the site of the leaving aqua ligand. Upon inclusion of the ligand within the cyclodextrin cavity, the positive charge on the $[AD\text{-}CNpyr]^+$ ligand is less accessible to form an ion pair with the $[Fe(CN)_5OH_2]^{3-}$ ions. In addition,

(29) (a) Macartney, D. H.; Warrack, L. J. *Can. J. Chem.* **1989**, *67*, 1774. (b) Foucher, D. A.; Macartney, D. H.; Warrack, L. J.; Wilson, J. P. *Inorg. Chem.* **1993**, *32*, 3425.

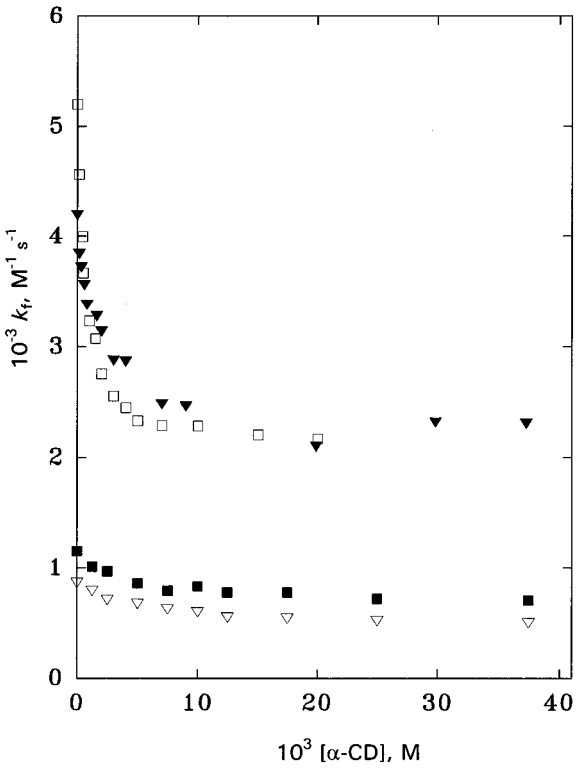

Figure 2. Dependences of the second-order rate constants, k_f, on α-cyclodextrin concentration for the reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion with the $[3CNpyr(CH_2)_{10}3CNpyr]^{2+}$ (□) and $[4CNpyr(CH_2)_{10}4CNpyr]^{2+}$ (▼) ligands and the $[Fe(CN)_5(3CNpyr(CH_2)_{10}3CNpyr]^{-}$ (■) and $[Fe(CN)_5(4CNpyr(CH_2)_{10}CNpyr)]^{-}$ (▽) complexes, at 25 °C (I = 0.10 M (NaCl)).

the included ligand is much larger than the free ligand, such that its donor nitrogen atom is accessible on a smaller portion of the surface of the cyclodextrin−ligand host−guest complex. The larger β-CD host cavity allows for deeper insertion, and therefore the limiting rate constants in the presence of high [β-CD] are generally somewhat lower relative to those measured at high [α-CD].

It was determined that, in the presence of excess α-CD, the rate constants for the formation of the $[Fe(CN)_5\{CNpyr(CH_2)_{10}CNpyr\cdot\alpha\text{-CD}\}]^{-}$ semirotaxanes were reduced to approximately half of the corresponding values measured in the absence of cyclodextrin (Table 3). This diminution of the rate constants is comparable to the decreases reported for the $[bpy(CH_2)_{10}bpy]^{2+}$ and $[pyz(CH_2)_{10}pyz]^{2+}$ ligands from previous studies in this laboratory[15,16] and is attributed to the steric bulk of the cyclodextrin host, as described above for the monocationic ligands. The α-cyclodextrin cavity also serves to isolate the charges on the ligand by allowing the hydrophobic decamethylene chain to assume a more extended configuration than that possible in the polar aqueous solution. The effect of this charge isolation by the cyclodextrin on k_f is analogous to the decrease in the rate constants for the reaction of the $[Fe(CN)_5OH_2]^{3-}$ ion with $[R(CH_2)_nR]^{2+}$ (R = 4,4′-bipyridine or pyrazine, n = 1−12) ligands as the number of methylene units (n) is increased.[15,16,29b] The net effect of the charge separation induced by cyclodextrin inclusion is the reduction of the effective charge on the entering ligand and therefore the outer-sphere ion-pair association constant, K_{os}, which will reduce the observed formation rate constant, k_f ($k_f = k_{-w}K_{os}$, where k_{-w} is the rate of aqua ligand dissociation from the $[Fe(CN)_5OH_2]^{3-}$ ion within the ion pair).[29]

The ligand substitution reactions of the $[Fe(CN)_5OH_2]^{3-}$ with the $[CNpyr(CH_2)_{10}CNpyr]^{2+}$ ligands were also studied using a pseudo-first-order excess of the $[Fe(CN)_5OH_2]^{3-}$ ion, resulting in the observation of two distinguishable consecutive first-order processes, corresponding to the formations of the monomeric $[Fe(CN)_5(CNpyr(CH_2)_{10}CNpyr)]^{-}$ (eq 7) and dimeric $[(NC)_5Fe(CNpyr(CH_2)_{10}CNpyr)Fe(CN)_5]^{4-}$ ions (eq 10). The addition

$$[Fe(CN)_5OH_2]^{3-} + [Fe(CN)_5(CNpyr(CH_2)_{10}CNpyr)]^{-} \xrightarrow{k_{f2}^0} [(NC)_5Fe(CNpyr(CH_2)_{10}CNpyr)Fe(CN)_5]^{4-} \quad (10)$$

of α-cyclodextrin resulted in a similar degree of reduction in the rate constants for the formation of the monomeric $[Fe(CN)_5(CNpyr(CH_2)_{10}CNpyr)]^{-}$ ion as observed using a pseudo-first-order excess of the ligand. The rate constants for the formation of the dimeric $[(NC)_5Fe(CNpyr(CH_2)_{10}CNpyr)Fe(CN)_5]^{4-}$ ion (eq 11) exhibit a smaller diminution upon

$$[Fe(CN)_5OH_2]^{3-} + [Fe(CN)_5\{CNpyr(CH_2)_{10}CNpyr\cdot\alpha\text{-CD}\}]^{-} \xrightarrow{k_{f2}^{CD}} [(NC)_5Fe\{CNpyr(CH_2)_{10}CNpyr\cdot\alpha\text{-CD}\}Fe(CN)_5]^{4-} \quad (11)$$

addition of α-CD (Figure 2). The observed second-order rate constants for the second step may be expressed in terms of the rate constants k_{f2}^0 and k_{f2}^{CD} and the inclusion stability constant for the semirotaxane, K_{ML} (eq 12). The rate and equilibrium

$$k_{f2}^{obs} = \frac{k_{f2}^0 + k_{f2}^{CD}K_{ML}[CD]}{1 + K_{ML}[CD]} \quad (12)$$

constants, calculated from a nonlinear least-squares fit of the data to eq 12, are presented in Table 3.

The formation of the monomeric complex is considerably faster than that of the dimer, as the entering ligand bears a +2 charge, rather than a formal −1 charge when a $[Fe(CN)_5]^{3-}$ group is attached to the other end of the bridging ligand. The small effect of [α-CD] on the rate constant for the reaction of the $[Fe(CN)_5OH_2]^{3-}$ ion with the monomeric $[Fe(CN)_5(CNpyr(CH_2)_{10}CNpyr)]^{-}$ ion may be related to two compensating factors. In the absence of cyclodextrin, the noncoordinated cyanopyridinium group would be able to participate in intramolecular ion-pairing with the $[Fe(CN)_5]^{3-}$ center coordinated to the other end of the ligand. The presence of this negatively charged entity would inhibit ion-pair formation with the approaching $[Fe(CN)_5OH_2]^{3-}$ ion and therefore reduce the formation rate constant. With the semirotaxane as the entering ligand, the cyclodextrin would separate these charges and thereby increase the effective ion-pairing with the $[Fe(CN)_5OH_2]^{3-}$ ion, contributing to an increase in the observed rate constant. The net decrease observed in the rate constants for the second formation step indicates that the steric and electronic hindrances resulting from the cyclodextrin inclusion, referred to above, are therefore of slightly greater significance.

The kinetics of the dissociation of the ligands L^{n+} from the $[Fe(CN)_5L]^{(3-n)-}$ complexes were followed by the addition of an excess of dimethyl sulfoxide, which forms a very inert complex (eq 13).[30] Decreases in the ligand dissociation rate

$$[Fe(CN)_5L]^{(3-n)-} + DMSO \xrightarrow{k_d^0} L^{n+} + [Fe(CN)_5DMSO]^{3-} \quad (13)$$

constants are observed upon the additions of α- or β-CD to the

(30) Toma, H. E.; Malin, J. M.; Giesbrecht, E. *Inorg. Chem.* **1973**, *12*, 2084.

reaction solutions, resulting from the CD inclusions of the coordinated ligands (eq 14). Values of k_d^{CD} and of K_{ML} were

$$[Fe(CN)_5\{L\cdot CD\}]^{(3-n)-} + DMSO \xrightarrow{k_d^{CD}} \{L\cdot CD\}^{n+} + [Fe(CN)_5(DMSO)]^{3-} \quad (14)$$

determined for the $[AD\text{-}CNpyr]^+$ complexes by a nonlinear least-squares fit of the experimental rate constants k_d^{obs} to eq 15. The dissociation rate constants and activation parameters

$$k_d^{obs} = \frac{k_d^0 + k_d^{CD}K_{ML}[CD]}{1 + K_{ML}[CD]} \quad (15)$$

for the $[(NC)_5Fe(CNpyr(CH_2)_{10}CNpyr)]^-$ complexes and the corresponding semirotaxane $[Fe(CN)_5\{CNpyr(CH_2)_{10}CNpyr\cdot\alpha\text{-}CD\}]^-$ species were obtained experimentally (Tables 2 and 3). However, since these species are difficult to obtain without having an excess of free ligand which would compete for the cyclodextrin, the K_{ML} values were obtained instead from the kinetics of the formation of the dimer complexes (eqs 10−12).

The ligand dissociation reactions of substituted pentacyanoferrate(II) complexes occur by a dissociative mechanism.[30] Since the 4-position of a pyridinium ring allows the electron density of its substituent to resonance-couple directly to its positively charged nitrogen, the nitrile groups of the substituted 4-cyanopyridinium ligands are more electron deficient than those of the corresponding 3-cyanopyridinium ligands and thus are able to accept more π-back-bonding from the pentacyanoferrate(II) metal center. This greater stability of the Fe−N bond of the 4-substituted ligands is reflected both in their λ_{max} values and in their lower k_d^0 values relative to those of the 3-cyanopyridinium ligands (Tables 2 and 3). The inclusion of the hydrophobic adamantyl group by α- or β-CD was observed to decrease the rate constants for the dissociation of the $[Fe(CN)_5\{AD\text{-}CNpyr\cdot CD\}]^{2-}$ complexes by approximately 30%. The preferential solvation of the sixth ligand by cyclodextrin stabilizes the ground state through greater π-back-bonding from the metal, which results in a decrease in the rate constants for the $[Fe(CN)_5\{AD\text{-}CNpyr\cdot CD\}]^{2-}$ complexes.

The stability constants for cyclodextrin guest-host complexes have been known to be dependent on the nature and concentrations of ions, employed as electrolytes and buffers, and organic cosolvents,[31,32] and the latter factor may account for some of the differences in the values measured by the different techniques in this study. In the ligand dissociation kinetics studies, for example, the presence of 0.10 M dimethyl sulfoxide generally decreases the magnitude of the binding constant calculated for the coordinated ligand (Tables 2 and 3) compared with the values obtained from ^{1}H NMR studies (Table 1). We have previously observed that the binding constants for β-CD inclusion complexes of N-heterocyclic ligands decrease somewhat in the presence of DMSO, and this has been attributed to the competitive solvation of the ligands by DMSO and the cyclodextrin cavity.

Rotaxane Self-Assembly. The self-assembly of [2]rotaxanes of the type $[(NC)_5Fe\{R(CH_2)_nR\cdot\alpha\text{-}CD\}Fe(CN)_5]^{4-}$ (R = 4,4′-bipyridine or pyrazine)[14−16] have been shown to proceed by two possible routes, depending on the order of addition of the three components. The first route, resulting from the addition of the labile aquapentacyanoferrate(II) ion to the corresponding

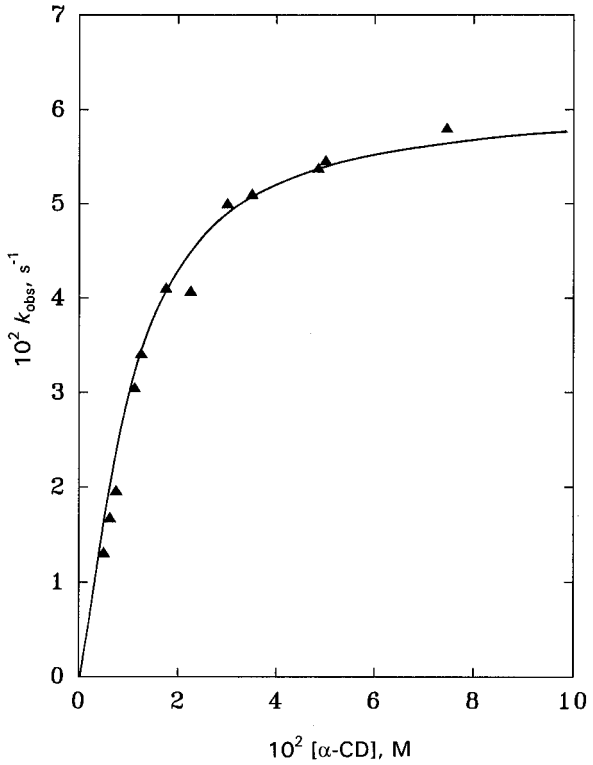

Figure 3. Plot of k_{obs} against [α-CD] for the self-assembly of the $[(NC)_5Fe\{4CNpyr(CH_2)_94CNpyr\cdot\alpha\text{-}CD\}Fe(CN)_5]^{4-}$ rotaxane at 25 °C (I = 0.10 M (NaCl)). The solid curve represents the fit of the data to eq 19, using the parameters presented in the text.

preassembled [2]pseudorotaxane species (eqs 3 and 8), is very rapid. A second, slower route involves the addition of cyclodextrin to the dimeric $[(NC)_5Fe(R(CH_2)_nR)Fe(CN)_5]^{4-}$ species. This pathway involves the rate-determining dissociation of a pentacyanoferrate(II) ion from the bridging ligand (eq 16), followed by the threading of the cyclodextrin by the free end of the coordinated ligand (eq 17) and the rapid recomplexation by an aquapentacyanoferrate(II) ion (eq 18).

$$[(NC)_5Fe(4CNpyr(CH_2)_94CNpyr)Fe(CN)_5]^{4-} \underset{k_{f2}^0}{\overset{k_{d2}^0}{\rightleftharpoons}} [(NC)_5Fe(4CNpyr(CH_2)_94CNpyr)]^- + [Fe(CN)_5OH_2]^{3-} \quad (16)$$

$$[(NC)_5Fe(4CNpyr(CH_2)_94CNpyr)]^- + \alpha\text{-CD} \overset{K_{ML}}{\rightleftharpoons} [(NC)_5Fe\{4CNpyr(CH_2)_94CNpyr\cdot\alpha\text{-}CD\}]^- \quad (17)$$

$$[Fe(CN)_5OH_2]^{3-} + [Fe(CN)_5\{CNpyr(CH_2)_9CNpyr\cdot\alpha\text{-}CD\}]^- \underset{k_{d2}^{CD}}{\overset{k_{f2}^{CD}}{\rightleftharpoons}} [(NC)_5Fe\{CNpyr(CH_2)_9CNpyr\cdot\alpha\text{-}CD\}Fe(CN)_5]^{4-} \quad (18)$$

The observed rate constant for the self-assembly by the last route may be related to the lability of the iron−nitrogen bond. Slower self-assembly processes were observed for the pentacyanoferrate(II) complexes with more inert N-heterocyclic head groups, such as 4,4′-bipyridine ($k = 4.0 \times 10^{-3}$ s^{-1})[15] and pyrazine ($k = 2.5 \times 10^{-4}$ s^{-1}),[16] which could be conveniently monitored by ^{1}H NMR spectroscopy. As a result of the greater lability of the iron−nitrogen bond in the complexes containing the 3- and 4-cyanopyridine head groups, measuring the kinetics of the self-assembly by this method was not feasible. It was observed previously, in the case of rotaxanes containing the

(31) (a) Rohrbach, R. P.; Rodriguez, L. J.; Eyring, E. M.; Wojcik, J. F. *J. Phys. Chem.* **1977**, *81*, 944. (b) Buvari, A.; Barcza, L. *Inorg. Chim. Acta* **1979**, *33*, L179.
(32) Schneider, H.-J.; Kramer, R.; Simova, S.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6442.

$[bpy(CH_2)_nbpy]^{2+}$ bridges, that with shorter polymethylene chains ($n = 8$ or 9) the rotaxane exhibits a slight bathochromic shift in the visible maximum, compared with the free dimer species.[15] In the present study, the dimer and rotaxane species prepared with the $[4CNpyr(CH_2)_94CNpyr]^{2+}$ ligand exhibited a shift in the λ_{max} from 556 to 564 nm, allowing for the monitoring of the rotaxane self-assembly by stopped-flow spectrophotometry. A solution of the dimer was mixed with a solution of excess cyclodextrin (containing a concentration of the rotaxane equal to that of the dimer, so as to maintain the iron concentration upon mixing), and the reaction was followed at 600 nm. The observed first-order rate constants increased with α-CD concentration, approaching a plateau at high [α-CD] (Figure 3).

On the basis of the self-assembly mechanism, the observed rate constant may be expressed as in eq 19, where k_{f2}^0, k_{f2}^{CD},

$$k_{obs} = \frac{k_{d2}^0 k_{f2}^{CD} K_{ML}[CD]}{k_{f2}^0 + k_{f2}^{CD} K_{ML}[CD]} \qquad (19)$$

k_{d2}^0, and K_{ML} are defined in eqs 16−18. The parameters k_{d2}^0 and K_{ML} were calculated from a nonlinear least-squares fit of the data (Figure 3). The rate constants $k_{f2}^0 = 870 \pm 15$ M^{-1} s^{-1} and $k_{f2}^{CD} = 680 \pm 20$ M^{-1} s^{-1} were measured at 25 °C for the $[4CNpyr(CH_2)_94CNpyr]^{2+}$ ion and employed in the calculation of K_{ML}. The calculated value of k_{d2}^0 is $(7 \pm 1) \times 10^{-2}$ s^{-1}, in reasonably good agreement with the rate constant of $(4.5 \pm 0.5) \times 10^{-2}$ s^{-1} determined from a study of the dissociation reaction of the $[(NC)_5Fe(4CNpyr(CH_2)_94CNpyr)Fe(CN)_5]^{4-}$ dimer complex in the presence of DMSO. The slight discrepancy in the values may result from medium effects or could reflect a slightly faster rate of dissociation of the first $[Fe(CN)_5]^{3-}$ unit relative to the second. The stability constant for the semirotaxane intermediate, K_{ML}, is calculated to be 93 ± 20 M^{-1}, smaller than the corresponding value 850 ± 150 M^{-1} for the $[Fe(CN)_5\{4CNpyr(CH_2)_{10}4CNpyr\cdot\alpha\text{-CD}\}]^-$ complex. This trend is consistent with that observed for the series of semirotaxanes containing the $[pyz(CH_2)_npyz]^{2+}$ bridging ligands (96 ± 16 M^{-1} for $n = 9$ and 770 ± 90 M^{-1} for $n = 10$).[16]

The present work is currently being extended to the preparation of [3]rotaxane complexes containing tetracationic bridging ligands of the type $[CNpyr(CH_2)_{10}bpy(CH_2)_{10}CNpyr]^{4+}$ (bpy = 4,4′-bipyridine), which give rise to the possibility of orientational isomers involving the two cyclodextrins. Preliminary ^1H NMR studies of the two self-assembly routes indicate that the pathway involving the dimeric iron complex leads to a nonstatistical distribution of orientational isomers. Mechanisms under consideration involve preferential cyclodextrin orientations in either the semirotaxane formations or the passage of the cyclodextrin over the central 4,4′-bipyridinium group.

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