α- and β-Cyclodextrin Rotaxanes of μ-Bis(4-pyridyl)bis[pentacyanoferrate(II)] Complexes

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The kinetics and mechanism of the self-assemblies of α- and β-cyclodextrin (CD) [2]rotaxanes, $[(NC)_5Fe\{pyRpy\cdot CD\}Fe(CN)_5]^{6-}$, containing pentacyanoferrate(II)-stoppered 4,4′-bis(pyridyl) threads pyRpy (R = −CH═CH−, −N═N−, −CH═N−N═CH−, and $-C(CH_3)═N-N═C(CH_3)-$) have been investigated in aqueous solution by using visible and ^{1}H NMR spectroscopy. The rotaxanes may be formed rapidly by the addition of the $[Fe(CN)_5OH_2]^{3-}$ ion to the CD-included pyRpy thread or slowly by the addition of an excess of CD to the dimeric $[(NC)_5Fe(pyRpy)Fe(CN)_5]^{6-}$ complex. In the latter method, the mechanism involves a rate-determining dissociation of a $[Fe(CN)_5]^{3-}$ center to form the monomeric complex, which subsequently includes the coordinated pyRpy in the CD cavity to yield the semirotaxane, which is rapidly recomplexed by the $[Fe(CN)_5OH_2]^{3-}$ ion, generating the [2]rotaxane. Rate and activation parameters and CD inclusion stability constants have been determined for the ligand substitution reactions involving the formations and dissociations of the semirotaxanes and rotaxanes. The extents of the decreases in the formation (k_f) and dissociation (k_d) rate constants upon CD inclusions of the free and coordinated ligands, respectively, are related to the natures of the CD hosts and the R linkage on the pyRpy guests. The semirotaxanes and rotaxanes exhibit significant bathochromic shifts in their visible MLCT transitions compared with the corresponding monomeric and dimeric iron complexes. A correlation between the extent of the decrease in k_d and the change in the MLCT energy upon α-CD inclusions of $[Fe(CN)_5L]^{3-}$, where L is an aromatic N-heterocyclic 4-Rpy or pyRpy ligand, has been observed.

Introduction

A supramolecular complex[1] comprised of a cyclic molecular bead threaded by a linear chain that is stoppered by bulky end units, which prevent the complex from dissociating into its cyclic and linear molecular components, is termed a rotaxane.[2] A variety of [2]rotaxanes ([*n*] designates the number of cyclic and linear components) have been assembled using a number of cyclic components,[3] including 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.[4] These cyclic hosts possess hydrophobic interior cavities and hydrophilic rims bearing primary and secondary hydroxyl groups. Pseudorotaxanes, in which the end units are not sufficiently bulky to prevent the dissociation of the cyclic and linear components, and rotaxanes of cyclodextrins have been prepared using a variety of organic[3,5−7] and transition metal complex[3,8−12] end groups. Cobalt(III) amine[8] and, more recently, cob(III)alamin[9] have been used to stopper polymethylene and α,ω-diaminopolymethylene chains, respectively. These complexes have generally been prepared by reacting a semirotaxane (bearing one metal stopper) with a second metal complex.

We have reported the results of kinetic and spectroscopic investigations of the mechanism of the self-assembly, in aqueous solution, of a series of stable α-cyclodextrin rotaxanes of the type $[(NC)_5Fe\{R(CH_2)_nR\cdot\alpha\text{-CD}\}Fe(CN)_5]^{4-}$, where the linear thread is a dicationic bridging ligand of the type $[R(CH_2)_nR]^{2+}$ (n = 8−12) and R is 4,4′-bipyridinium,[10] pyrazinium,[11] or 3-

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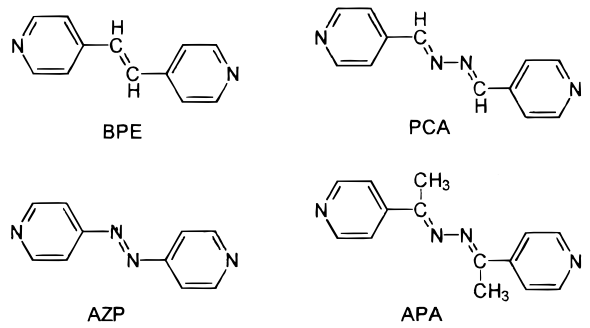
Chart 1



and 4-cyanopyridinium[12] entities. These species represent metal-stopped rotaxane complexes that will self-assemble irrespective of the order of the addition of the α-CD, bridging ligand, and $[Fe(CN)_5]^{3-}$ components. A third method of rotaxane self-assembly, termed "slippage",[13−15] results when the threading of the linear components only occurs efficiently at elevated temperatures as the diameters of the host cavity and the end group of the host are closely matched in size.[5−7]

In this paper we report the results of kinetic and spectroscopic studies of the reactions in the mechanism of the self-assembly of α- and *β*-cyclodextrin rotaxanes of the type $[(NC)_5Fe\{pyRpy\cdot CD\}Fe(CN)_5]^{6-}$, where pyRpy are neutral bridging 4,4′-bis-(pyridine) ligands with a variety of functional groups connecting the 4 and 4′ pyridine carbons (Chart 1). The *trans*-1,2-bis(4-pyridyl)ethylene ligand (BPE) has frequently been employed as a conjugated bridging ligand in the study of inner-sphere and intervalence electron transfer between transition metal centers.[16] The 4,4′-azopyridine ligand (AZP) has been employed as a bridging ligand between ruthenium amines and porphyrins.[17] The novel 4-acetylpyridine azine (APA)and 4-pyridinecarboxaldehyde azine (PCA) ligands were prepared using a recently reported preparation for the analogous bis(2-pyridyl) compound.[18] Cyclodextrin inclusion complexes with azo dye guests have been studied extensively using a variety of spectroscopic techniques.[19] There have also been several reports of cyclodextrin [2] and [3]rotaxanes, polyrotaxanes, and catenanes prepared using threads containing biphenyl,[20] stilbene,[21] and azobenzene dye[22] groups.

The stability constants for the {pyRpy·CD} inclusion complexes and the semirotaxanes $[Fe(CN)_5\{pyRpy\cdot CD\}]^{3-}$ have been determined by means of UV−visible and ^{1}H NMR chemical shift titrations, as well as ligand substitution kinetic studies. The kinetics and mechanisms of the formation and ligand dissociation reactions of the semirotaxane $[(NC)_5Fe\{pyRpy\cdot CD\}]^{3-}$ and the self-assembly of the rotaxanes have been studied by using visible and ^{1}H NMR spectroscopy.

Experimental Section

Materials. The α- and *β*-cyclodextrins (Aldrich) were dried at 80 °C under vacuum for at least 12 h prior to use. Sodium amminepentacyanoferrate(II) hydrate, $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$, was prepared by a literature method[23] and recrystallized from concentrated ammonia/methanol solution. The $[Fe(CN)_5OH_2]^{3-}$ was generated in solution by the rapid aquation of the amine salt and was generally kept at low concentrations ($<10^{-4}$ M) when possible to minimize dimerization processes. When higher concentrations were necessary, the concentration of the $[Fe(CN)_5OH_2]^{3-}$ ion was determined spectrophotometrically ($\lambda_{max} = 444$ nm, $\epsilon = 660$ M^{-1} cm^{-1})[23b] immediately prior to reaction. The 4-pyridinecarboxaldehyde, 4-acetylpyridine, 4-aminopyridine, hydrazine hydrate, and *trans*-1,2-bis(4-pyridyl)ethylene (BPE) were used as received (Aldrich). The 4,4′-azopyridine (AZP) was prepared from the reactions of 4-aminopyridine with sodium hypochlorite by the method of Launay et al.[17a] The 4-pyridinecarboxaldehyde azine (PCA) and 4-acetylpyridine azine (APA) compounds were prepared by adapting the method of Kesslen and Euler,[18] reported for the 2-pyridyl analogues.

(a) PCA. Yield 41%. Mp: 182−184 °C. Anal. Calcd for $C_{12}H_{10}N_4$: C, 68.56; H, 4.79; N, 26.65. Found: C, 68.15; H, 4.63; N, 26.72. ^{1}H NMR (D_2O): δ 8.71(d, 4 H, H2, $J_{2,3} = 5.8$ Hz), 8.67 (s, 2 H, C*H*═N), 7.87 (d, 4H, H3) ppm.

(b) APA. Yield 43%. Mp: 114−116 °C. Anal. Calcd for $C_{14}H_{14}N_4$: C, 70.58; H, 5.92; N, 23.51. Found: C, 69.84; H, 5.89; N, 23.20. ^{1}H NMR (D_2O): δ 8.67 (d, 4H, H2, $J_{2,3} = 4.6$ Hz), 7.83 (dd, 4H, H3, $J_{3,2} = 4.6$, $J_{3,2'} = 2.0$ Hz), 2.30 (s, 6H, CH_3) ppm.

Physical Measurements. The ^{1}H NMR spectra were recorded on Bruker AC-200 and Bruker AM-400 instruments in D_2O, employing the residual solvent proton signal as the reference. The kinetics measurements on the rapid reactions were performed by using a SX-17MV stopped−flow spectrofluorometer (Applied Photophysics). Pseudo-first-order conditions of excess ligand were generally employed except in studies of the formation of dimeric species, in which case the $[Fe(CN)_5OH_2]^{3-}$ species was present in excess. In the study of the formation of the iron dimer complex with PCA, a pseudo-first-order excess of a freshly prepared $[Fe(CN)_5OH_2]^{3-}$ ion solution was employed, and the kinetic traces were fit to two consecutive first-order reactions using the Applied Photophysics software. The spectrophotometric titrations and the kinetics of the slower ligand substitution reactions were carried out by using a Hewlett-Packard 8452A spectophotometer. 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 nine replicate experiments performed for the stopped−flow measurements and one experiment for the ligand substitution reactions. The temperatures of the reactions were maintained to ±0.1 °C over the range 10−35 °C by means of external circulating water baths, and the ionic strength was held at 0.10 M by using added NaCl.

The stability constants for the cyclodextrin inclusion complexes and the kinetics of the self-assembly of the rotaxanes were determined from ligand substitution kinetics data and ^{1}H NMR titrations by applying nonlinear least-squares and simplex optimization programs to the equations for 1:1 and 1:2 guest−host models, as described previously.[24] For the kinetics of the dissociation reactions of the $[Fe(CN)_5L]^{3-}$ complexes (L = BPE, AZP, and APA), an excess of the ligand L was

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present to ensure formation of the monomeric complex. In the presence of cyclodextrin, both the free ligand (L) and the metal complex (ML) will form inclusion complexes with the CD, and a competitive 1:1 binding model is used to fit the data and extract values for K_L^{CD} for

$$L + CD \overset{K_L^{CD}}{\rightleftharpoons} \{L\cdot CD\} \quad (1)$$

and K_{ML}^{CD} for

$$[Fe(CN)_5L]^{3-} + CD \overset{K_{ML}^{CD}}{\rightleftharpoons} [Fe(CN)_5\{L\cdot CD\}]^{3-} \quad (2)$$

The concentration of the unbound cyclodextrin was determined by solving the polynomial

$$0 = [CD]^3 + \left(\frac{K_L^{CD} + K_{ML}^{CD}}{K_L^{CD}K_{ML}^{CD}} + [L]_T + [ML]_T - [CD]_T\right)[CD]^2 + \left(\frac{1}{K_L^{CD}K_{ML}^{CD}} + \frac{[L]_T}{K_{ML}^{CD}} + \frac{[ML]_T}{K_L^{CD}} - \frac{[CD]_T}{K_L^{CD}} - \frac{[CD]_T}{K_{ML}^{CD}}\right)[CD] - \frac{[CD]_T}{K_L^{CD}K_{ML}^{CD}} \quad (3)$$

The concentrations of the inclusion complexes {L·CD} and M{L·CD} were calculated from [CD] using

$$[\{L\cdot CD\}] = \frac{[L]_T}{1 + (K_L^{CD} + [CD])^{-1}} \quad (4)$$

and

$$[M\{L\cdot CD\}] = \frac{[ML]_T}{1 + (K_{ML}^{CD} + [CD])^{-1}} \quad (5)$$

and the concentrations of the unbound ligand and metal complex were determined by $[L] = [L]_T - [\{L\cdot CD\}]$ and $[ML] = [ML]_T - [M\{L\cdot CD\}]$.

Results

Ligand−Cyclodextrin Inclusion Complexes. The addition of α- or β-cyclodextrin to aqueous solutions of the pyRpy ligands (L) in Chart 1 results in the formation of guest−host inclusion complexes of varying stability (eq 1). The stability constants (K_L^{CD}) for the inclusion complexes have been determined by a variety of methods, including visible and ^{1}H NMR spectroscopy and from the kinetics of ligand substitution reactions of the pyRpy ligands with the $[Fe(CN)_5OH_2]^{3-}$ ion.

From spectrophotometric titrations of AZP ($\lambda_{max} = 446$ nm) with the cyclodextrins, stability constants of 304 ± 26 and 496 ± 88 M^{-1} were obtained for the {AZP·α-CD} ($\lambda_{max} = 463$ nm) and {AZP·β-CD} ($\lambda_{max} = 453$ nm) inclusion complexes, respectively. In D_2O, the corresponding stability constant for the {AZP·α-CD} complex was determined to be 255 ± 12 M^{-1}. In a similar manner, the changes in the ^{1}H NMR chemical shifts of the aromatic H2 and H3 ligand protons (not masked by CD resonances) upon addition of the cyclodextrins may be employed to determine the values for the stability constants in D_2O (Table 1).[24]

Most of the ligands in this study exhibited 1:1 binding with both α- and β-cyclodextrin except for PCA and APA, which exhibits both 1:1 and 2:1 binding with α-CD:

$$\{pyRpy\cdot\alpha\text{-}CD\} + \alpha\text{-}CD \overset{K_L^{2CD}}{\rightleftharpoons} \{\alpha\text{-}CD\cdot pyRpy\cdot\alpha\text{-}CD\} \quad (6)$$

Nonlinear regression of equations for APA with α-cyclodextrin yielded the stability constants presented in Table 1. Nonlinear regressions of the equations for 1:1 and 1:2 guest−host models[24] provided the inclusion stability constants K_L^{CD} and K_L^{2CD} (Table 1) and limited chemical shifts for the guest ligands with α- and β-cyclodextrin.

Kinetics of Pentacyanoferrate(II) Complex Formation and Dissociation. The addition of an excess of a pyRpy ligand to a solution of the $[Fe(CN)_5OH_2]^{3-}$ ion results in the rapid formation of the substituted complex $[Fe(CN)_5pyRpy]^{3-}$. The formation of this complex is manifested in changes to the visible spectrum of the metal complex, with the emergence of an intense metal-to-ligand (MLCT) band, and the ^{1}H NMR spectrum of the ligand upon complexation. These spectra are also affected by the presence of α- or β-cyclodextrins, resulting in bathochromic shifts in the MLCT band in the visible spectrum (Table 1) and chemical shifts changes in the ^{1}H NMR spectrum upon inclusion of the coordinated pyRpy ligands in the cyclodextrin cavities.

The rate constants k_f for the ligand substitution reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion with the pyRpy ligands,

$$[Fe(CN)_5OH_2]^{3-} + pyRpy \xrightarrow{k_f} [Fe(CN)_5pyRpy]^{3-} \quad (7)$$

measured at 25.0 °C and $I = 0.10$ M (NaCl), are observed to decrease substantially in the presence of α- or β-cyclodextrins,

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

reaching limiting values of k_f^{CD} at high cyclodextrin concentrations. The dependence of the observed second-order rate constants for the substitution reaction may be expressed in terms of the specific rate constants k_f and k_f^{CD} and the stability constant for the cyclodextrin inclusion complex K_L^{CD}, as in the general form in

$$k^{obs} = \frac{k + k^{CD}K^{CD}[CD]}{1 + K^{CD}[CD]} \quad (9)$$

Nonlinear least-squares fits of the observed rate constants to eq 9 resulted in the rate and stability constants presented in Table 1, along with activation parameters corresponding to the rate constants k_f and k_f^{CD}. Because of the insolubility of PCA in water, the kinetics of its ligand substitution reactions were measured in the presence of a pseudo-first-order excess of the $[Fe(CN)_5OH_2]^{3-}$ ion. As a result, the rate of formation of the dimer $[(NC)_5Fe(PCA)Fe(CN)_5]^{6-}$,

$$[Fe(CN)_5OH_2]^{3-} + [Fe(CN)_5PCA]^{3-} \xrightarrow{k_{f2}} [(NC)_5Fe(PCA)Fe(CN)_5]^{6-} \quad (10)$$

was determined in addition to the rate constant for the monomer formation (eq 7). The rate constant for the formation of the dimer, $k_{f2} = 158 \pm 10$ M^{-1} s^{-1}, is much smaller than the corresponding value for the monomeric species, $k_f = 680 \pm 80$ M^{-1} s^{-1}, because of electrostatic inhibition resulting from the −3 charge on the entering ligand ($k_{f2} = 95 \pm 8$ M^{-1} s^{-1} for BPE[25]).

In the presence of the cyclodextrins the rate constants decrease as a result of the inclusion of the bridging ligand (eq 2), with a stability constant K_{ML}^{CD}. At high cyclodextrin concentrations, the observed second-order rate constant becomes very small and approaches a limiting value of k_{f2}^{CD} for the formation of the

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Table 1. Visible Maxima, Kinetic and Activation Parameters, and Cyclodextrin Inclusion Stability Constants Associated with Ligand Substitution Reactions of the $[Fe(CN)_5OH_2]^{3-}$ Ion in Aqueous Solution at 25.0 °C and $I = 0.10$ M (NaCl)

	ligands			
parameter	BPE	AZP	PCA	APA
$Fe(CN)_5L^{3-}$ λ_{max}, nm	460	596	508	448
$(Fe(CN)_5\{L\cdot CD\}^{3-})^a$ λ_{max}, nm	496 (α)	698 (α)	536 (α)	456 (α)
	478 (β)	644 (β)	518 (β)	458 (β)
k_f, M^{-1} s^{-1}	757 ± 19[b]	570 ± 12	680 ± 80	618 ± 12
$\Delta H_f^{\ddagger}$, kJ mol^{-1}	65 ± 5[b]	74 ± 1		75 ± 4
$\Delta S_f^{\ddagger}$, J K^{-1} mol^{-1}	28 ± 14[b]	55 ± 4		61 ± 13
k_f^{CD}, M^{-1} s^{-1}	33 ± 19 (α)	142 ± 11 (α)	376 ± 50 (α)	304 ± 45 (α)
	134 ± 11 (β)[b]	170 ± 31 (β)	220 ± 40 (β)	139 ± 19 (β)
k_f^{2CD}, M^{-1} s^{-1}			142 ± 25 (α)	0 ± 30 (α)
$\Delta H_f^{CD\ddagger}$, kJ mol^{-1}		74 ± 1 (α)	75 ± 2 (α)	
		73 ± 5 (β)	68 ± 5 (β)	
$\Delta S_f^{CD\ddagger}$, J K^{-1} mol^{-1}		44 ± 1 (α)	50 ± 6 (α)	
		45 ± 15 (β)	30 ± 14 (β)	
K_L^{CD}, M^{-1}	33 ± 2 (α)	294 ± 36 (α)	2100 ± 250 (α)	21 ± 10 (α)[c]
	51 ± 2 (α)[c]	273 ± 5 (α)[c]	70 ± 20 (α)[d]	4 ± 2 (α)[c,d]
	203 ± 10 (β)[b]	304 ± 26 (α)[e]	161 ± 36 (β)	24 ± 8 (α)
	240 ± 37 (β)[b,c]	255 ± 12 (α)[f]		6 ± 2 (α)[d]
		440 ± 109 (β)		327 ± 41 (β)
		310 ± 30 (β)[c]		567 ± 60 (β)[c]
		496 ± 88 (β)[e]		
$10^3 k_d$, s^{-1}	0.80 ± 0.08	0.59 ± 0.01	0.59 ± 0.06	0.71 ± 0.07
$\Delta H_d^{\ddagger}$, kJ mol^{-1}	123 ± 7	120 ± 2	117 ± 1	115 ± 3
$\Delta S_d^{\ddagger}$, J K^{-1} mol^{-1}	108 ± 21	96 ± 5	84 ± 4	82 ± 10
$10^3 k_d^{CD}$, s^{-1}	0.10 ± 0.02 (α)	0.028 ± 0.003 (α)	0.17 ± 0.02 (α)	0.70 ± 0.01 (α)
	0.26 ± 0.02 (β)	0.051 ± 0.005 (β)	0.46 ± 0.05 (β)	0.27 ± 0.02 (β)
$\Delta H_d^{CD\ddagger}$, kJ mol^{-1}		112 ± 6 (α)		
		116 ± 4 (β)		
$\Delta S_d^{CD\ddagger}$, J K^{-1} mol^{-1}		42 ± 17 (α)		
		76 ± 12 (β)		
K_{ML}^{CD}, M^{-1}	71 ± 16 (α)	1290 ± 80 (α)	750 ± 130 (α)	800 ± 220 (β)
	54 ± 3 (α)[g]	1000 ± 200 (α)[h]	467 ± 28 (α)[g]	760 ± 43 (β)[g]
	209 ± 44 (β)	940 ± 73 (α)[g]	279 ± 64 (β)	
	280 ± 35 (β)[c]	145 ± 50 (β)	189 ± 24 (β)[g]	
	205 ± 12 (β)[g]	200 ± 40 (β)[h]		
		146 ± 6 (β)[g]		

[a] [α-CD] = 0.10 M; [β-CD] = 0.015 M. [b] Reference 24. [c] Determined by ^{1}H NMR chemical shift titration in D_2O. [d] K_L^{2CD}. [e] Determined from a spectrophotometric titration of L with CD in H_2O. [f] Determined from a spectrophotometric titration of L with CD in D_2O. [g] Determined from the kinetics of the self-assembly of the CD rotaxane from the dimer $[(NC)_5Fe(L)Fe(CN)_5]^{6-}$. [h] Determined from a spectrophotometric titration of $[Fe(CN)_5AZP]^{3-}$ with CD in H_2O.

rotaxane complex $[(NC)_5Fe\{PCA\cdot\alpha\text{-CD}\}Fe(CN)_5]^{6-}$:

$$[Fe(CN)_5OH_2]^{3-} + [Fe(CN)_5\{PCA\cdot\alpha\text{-CD}\}]^{3-} \xrightarrow{k_{f2}^{CD}} [(NC)_5Fe\{PCA\cdot\alpha\text{-CD}\}Fe(CN)_5]^{6-} \quad (11)$$

Fits of the kinetic data to eq 2 yield rate constants $k_{f2}^{CD} = 45 \pm 4$ M^{-1} s^{-1} (α-CD) and 69 ± 6 M^{-1} s^{-1} (β-CD) and stability constants $K_{ML}^{CD} = 750 \pm 130$ M^{-1} (α-CD) and 279 ± 64 M^{-1} (β-CD).

The rate constants for the slow dissociation of the coordinated pyRpy ligands from the iron(II) center may be determined by adding an excess of dimethyl sulfoxide (DMSO, 0.10 M), which rapidly reacts with the resulting five-coordinate $[Fe(CN)_5]^{3-}$ ion intermediate, yielding the very stable and colorless $[Fe(CN)_5DMSO]^{3-}$ ion:

$$[Fe(CN)_5pyRpy]^{3-} + DMSO \xrightarrow{k_d} [Fe(CN)_5DMSO]^{3-} + pyRpy \quad (12)$$

The inclusion of the coordinated pyRpy ligand in the cyclodextrin cavity results in an increased inertness of the Fe−N bond, and the dissociation rate constant decreases to a limiting value of k_d^{CD},

$$[Fe(CN)_5\{pyRpy\cdot CD\}]^{3-} + DMSO \xrightarrow{k_d^{CD}} [Fe(CN)_5DMSO]^{3-} + \{pyRpy\cdot CD\} \quad (13)$$

The limiting rate constant and the inclusion stability constant, along with activation parameters associated with the rate constants k_d and k_d^{CD}, were determined from fits of the observed dissociation rate constants to eq 9 and are presented in Table 1. The inclusion stability constant for the coordinated BPE ligand, K_{ML}^{CD}, was also determined from ^{1}H NMR chemical shift titration with β-CD and yielded a similar value.

The rate constant k_d for the dissociation of the bridging PCA ligand from the dimer complex (Table 1) was found to be very similar to the values measured for the monomeric species. By comparison, the dissociation of the included bridging ligand in the α- and β-CD rotaxanes proceeds with a considerably diminished rate constant k_d^{rot} (Table 1).

$$[(NC)_5Fe(PCA)Fe(CN)_5]^{6-} + DMSO \xrightarrow{k_{d2}} 2[Fe(CN)_5DMSO]^{3-} + PCA \quad (14)$$

$$[(NC)_5Fe\{PCA\cdot CD\}Fe(CN)_5]^{6-} + DMSO \xrightarrow{k_d^{rot}} 2[Fe(CN)_5DMSO]^{3-} + \{PCA\cdot CD\} \quad (15)$$

Table 2. Spectroscopic and Kinetic Parameters Associated with the Self-Assembly of the [2]Rotaxane $[(NC)_5Fe\{L\cdot CD\}Fe(CN)_5]^{6-}$ [L = BPE, AZP, PCA, APA] from the Dimer $[(NC)_5Fe(L)Fe(CN)_5]^{6-}$ and α- or β-CD at 25 °C, I = 0.10 M NaCl

	ligands			
parameters	BPE	AZP	PCA	APA
λ_{max}, nm (dimer)	472	624	512	450
λ_{max}, nm (α-CD rotaxane)[a]	504	742	552	*b*
$\Delta\delta$,[c] ppm, H2, H3 (α-CD)	0.24, 0.38	0.19, 0.52	0.21, 0.25	*b*
10^3k_{lim}, s^{-1} (α-CD)	0.63 ± 0.03[d]	0.58 ± 0.01[d]	0.86 ± 0.02[d]	*b*
K_{ML}^{CD}, M^{-1} (α-CD)	54 ± 3[d]	940 ± 73[d]	467 ± 28[d]	*b*
λ_{max}, nm (β-CD rotaxane)[e]	496	670	528	458
$\Delta\delta$,[c] ppm, H2, H3 (β-CD)	0.13, 0.01	010, 0.12	0.14, 0.07	0.09, 0.09
10^3k_{lim}, s^{-1} (β-CD)	0.79 ± 0.03[f]	0.60 ± 0.02[d]	0.85 ± 0.06[d]	0.87 ± 0.01[f]
K_{ML}^{CD}, M^{-1} (β-CD)	205 ± 12[f]	148 ± 6[d]	189 ± 24[d]	760 ± 43[f]

[a] [α-CD] = 0.15 M. [b] No rotaxane is formed with α-CD. [c] ^{1}H NMR chemical shift difference between the symmetry-related pyridine H2 and H3 proton resonances for the rotaxane complexes. [d] Determined from the kinetics of the self-assembly reaction of the rotaxane $[(NC)_5Fe\{L\cdot CD\}Fe(CN)_5]^{6-}$ from the dimer $[(NC)_5Fe(L)Fe(CN)_5]^{6-}$ in the presence of CD in H_2O (spectophotometrically). [e] [β-CD] = 0.015 M. [f] Determined from the kinetics of the self-assembly reaction of the rotaxane $[(NC)_5Fe\{L\cdot CD\}Fe(CN)_5]^{6-}$ from the dimer $[(NC)_5Fe(L)Fe(CN)_5]^{6-}$ in the presence of CD in D_2O (^{1}H NMR).

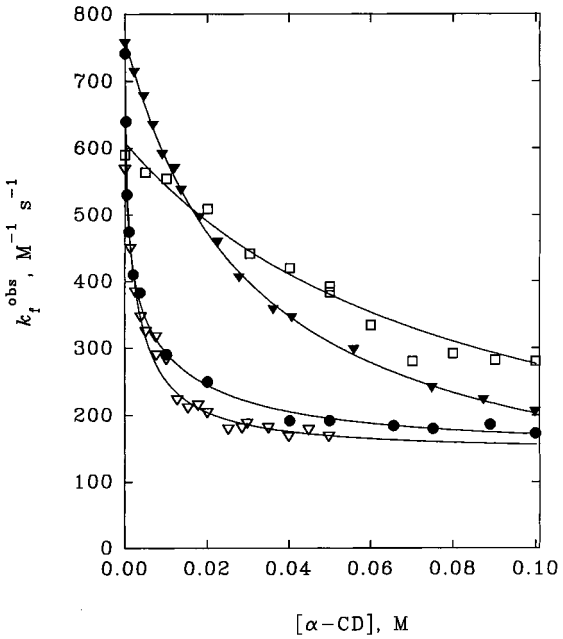
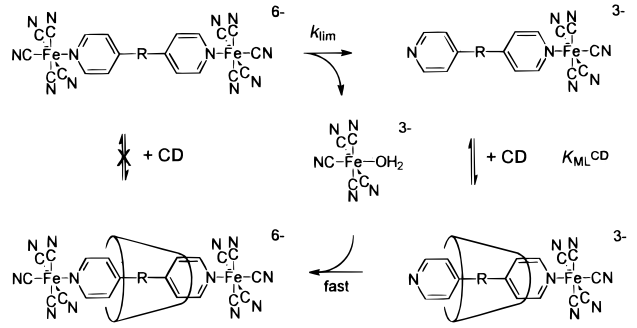


Figure 1. Dependence of k_f^{obs} on [α-CD] for the ligand substitution reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion with (●) PCA, (▽) AZP, (▼) BPE, and (□) APA (0.754 mM) at 25.0 °C (I = 0.10 M (NaCl)). The solid curves represent the fit to the kinetics data using the parameters from Table 1.

Solvatochromism of MLCT Transitions. All of the $[Fe(CN)_5pyRpy]^{3-}$ and $[(NC)_5Fe(pyRpy)Fe(CN)_5]^{6-}$ complexes with the bis(4-pyridyl) ligands exhibit intense metal-to-ligand charge transfer (MLCT) bands in the visible spectrum (Tables 1 and 2). The wavelength maxima at which these MLCT bands occur are related to the extent of the π-back-bonding from the filled metal t_{2g} orbitals to the empty ligand π* orbitals. The visible spectra of the semirotaxane ($[Fe(CN)_5\{pyRpy\cdot CD\}]^{3-}$) and rotaxane ($[(NC)_5Fe\{pyRpy\cdot CD\}Fe(CN)_5]^{6-}$) species exhibit bathochromic shifts in their MLCT bands with respect to the corresponding monomeric (Table 1) and dimeric (Table 2) pentacyanoferrate(II) complexes. The lowering of the energies of MLCT bands results from the inclusion of the N-heterocyclic ligands in the cyclodextrin cavities. The magnitudes of the shifts are dependent on the size of the cyclodextrin cavity and the nature of the R linkage in pyRpy ligands.

Similar behavior in the MLCT band energies is observed when these complexes are placed in aqueous/organic solvent mixtures. With the $[Fe(CN)_5AZP]^{3-}$ complex, for example, the MLCT band undergoes a bathochromic shift to a wavelength similar to that of $[Fe(CN)_5\{AZP\cdot CD\}]^{3-}$ (698 nm) when the solvent system is 40% aqueous DMSO or DMF, 70% aqueous acetone, or 80% aqueous methanol.

Scheme 1



Rotaxane Self-Assembly. In addition to preparing the rotaxane species rapidly by adding an excess of the $[Fe(CN)_5OH_2]^{3-}$ stopper to a solution of the {pyRpy·CD} inclusion complex, the rotaxane may also be formed more slowly by the reaction of the $[(NC)_5Fe(pyRpy)Fe(CN)_5]^{6-}$ complex with an excess of α- or β-cyclodextrin (Scheme 1). The kinetics of these self-assembly processes may be monitored by using either visible (changes in MLCT bands (Table 2)) or ^{1}H NMR spectroscopy (Figure 2). The symmetry-related aromatic proton resonances of the bridging pyRpy ligand in the ^{1}H NMR spectrum of the dimer complex are separated into pairs of doublets as the rotaxane is formed.

The rate constants for the rotaxane formations were observed to be dependent on the concentration of CD, approaching a limiting value, k_{lim}, at higher concentrations of cyclodextrin. The dependence of the observed rate constant for self-assembly may be expressed in terms of rate and stability constants, as in eq 9, where $k = 0$ and $k^{CD} = k_{lim}$. Double-reciprocal plots of $1/k_{obs}$ against 1/[CD], as shown in Figure 3, yielded values for the rate constant k_{lim} from the intercept and the stability constant K_{ML}^{CD} from the ratio of the intercept to the slope (Table 2).

Discussion

The stability constants K_L^{CD} for the 1:1 guest/host inclusions of the pyRpy ligands in β-cyclodextrin exhibits (Table 1) the trend AZP > APA > BPE > PCA, with values falling in a relatively narrow range (200−700 M^{-1}). These stability constants are within the range previously reported for 4,4′-bipyridine (170 ± 21 M^{-1}) and bis(4-pyridine) ligands with saturated bridges, 830 ± 81 M^{-1} for 1,2-bis(4-pyridyl)ethane and 3100

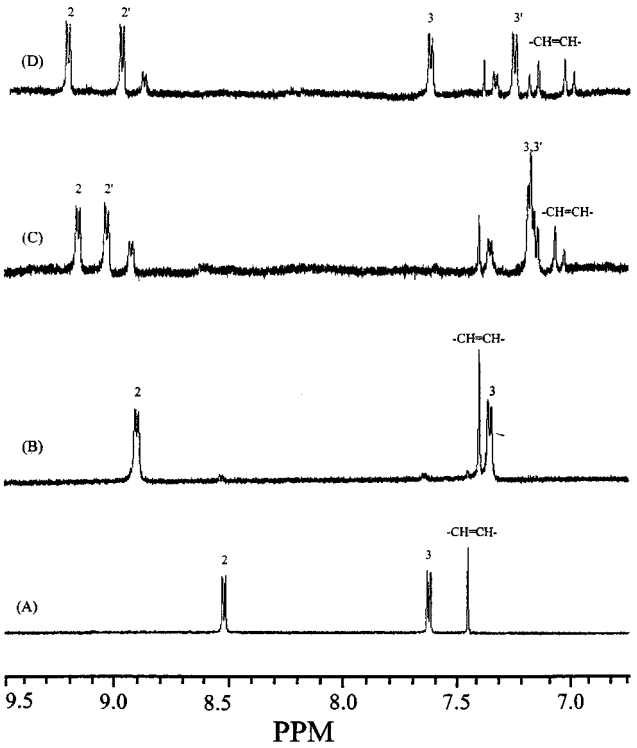


Figure 2. ^{1}H NMR spectra of (a) BPE, (b) $[(NC)_5Fe(BPE)Fe(CN)_5]^{6-}$, (c) $[(NC)_5Fe\{BPE{\cdot}\beta\text{-CD}\}Fe(CN)_5]^{6-}$ ($[\beta\text{-CD}] = 15$ mM), and (d) $[(NC)_5Fe\{BPE{\cdot}\alpha\text{-CD}\}Fe(CN)_5]^{6-}$ ($[\alpha\text{-CD}] = 50$ mM) in D_2O.

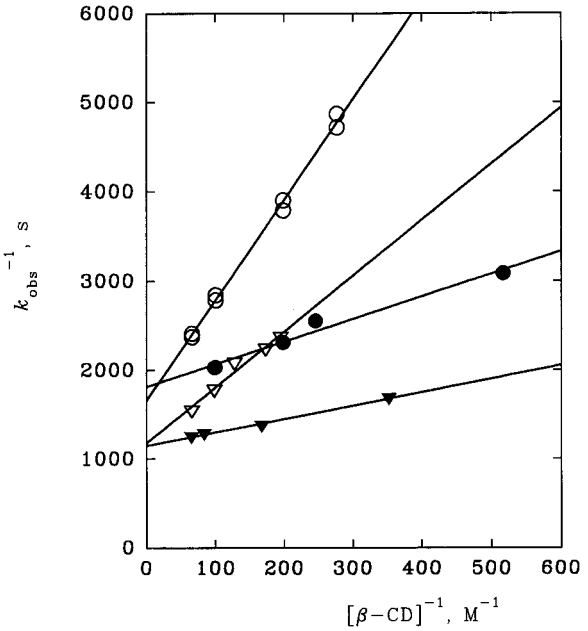


Figure 3. Plots of k_{obs}^{-1} against $[\beta\text{-CD}]^{-1}$ for the self-assembly of the rotaxane from the dimer $[(NC)_5Fe(L)Fe(CN)_5]^{6-}$ at 25 °C ($I = 0.10$ M (NaCl)). The ligands are (○) AZP, (●) BPE, (▽) PCA, and (▼) APA. The solid lines represent linear least-squares regressions of the kinetics data, using the parameters in Table 2.

$\pm$ 1700 M^{-1} for 1,3-bis(4-pyridyl)propane.[24] These data suggest that increased stability of the inclusion complex is afforded by increasing the length of the bridging group and increasing the flexibility of the bridge through saturation.[26] A somewhat different trend in K_L^{CD} is exhibited (Table 1) for the inclusion of the pyRpy ligands in α-cyclodextrin, PCA ≫ AZP > BPE > APA, with a much wider range (20−2100 M^{-1}) of stability constants. With the smaller cavity of the α-cyclodextrin, the steric demands of the pyridine ring and bridging group play a more dominant role in the magnitude of K_L^{CD} for α-CD than observed for β-CD. The AZP ligand, with the −N═N− azo linkage, is clearly favored by α-CD over the pyRpy ligands where R is −CH═CH− or $-CH_2CH_2-$ ($K_L^{CD} = 30 \pm 5$ M^{-1} for α-CD[24]). Large stability constants for α-CD inclusion complexes have also been reported for a number of azo dye molecules (10^3-10^4 M^{-1}),[17] which bear polar substituents at each end.

The PCA and APA ligands form both 1:1 and 1:2 guest/host inclusion complexes with α-cyclodextrin (Table 1). The nature of the binding differs between the two ligands in terms of the location of the first cyclodextrin. With PCA, the first α-CD moiety rests over the bridging group of the ligand, −C(H)═N−N═C(H)−, where it is tightly bound with $K_L^{CD} = 2100$ M^{-1}. The second α-CD molecule includes one of the pyridine groups, resulting in a much smaller value of K_L^{2CD} (70 M^{-1}). The methyl groups present in the bridging group of the APA ligand, $-C(CH_3)-N{=}N-C(CH_3)-$, prevent its full inclusion in the α-cyclodextrin cavity. As a result, both of the cyclodextrins are bound only to the pyridine rings, and the binding constants are low. The APA/α-CD system exhibits statistical binding, with a ratio K_L^{CD}/K_L^{2CD} of approximately 4. This is consistent with the sequential binding of the pyridines, with little or no interaction between the two cyclodextrin hosts. The stability constants presented in Table 1 indicate good agreement between values measured by visible and ^{1}H NMR titrations and values from ligand substitution kinetic measurements.

Inclusion of the bis(4-pyridyl) ligands in cyclodextrin results in a decrease in k_f, the rate constant for formation of the monomer $[Fe(CN)_5\{pyRpy{\cdot}CD\}]^{3-}$. This decrease is observed for both α- and β-CD and is caused by the steric hindrance introduced by the presence of the cyclodextrin. The ligands exhibit a larger range of k_f^{CD} values upon inclusion in α-CD than in β-CD, a result of the smaller cavity size of α-CD. Both of the reactions involving the BPE and AZP ligands show larger drops in k_f upon inclusion in α-CD than in β-CD because the tighter fit of α-CD results in greater steric interference. The PCA and APA ligands exhibit different binding behavior with α-cyclodextrin. Upon inclusion by one α-CD, both ligands show much smaller drops in k_f than either with AZP or with BPE. With PCA this is a result of its longer length relative to either AZP or BPE such that the pyridine rings protrude further from the cyclodextrin cavity, lessening steric interference.

The k_f value for APA drops by exactly half upon its inclusion in one α-CD because one of the pyridines is now completely included and can no longer bind to the $[Fe(CN)_5]^{3-}$ center. The inclusion of PCA in a second α-CD causes k_f to drop by half from its value upon inclusion in the first α-CD because one of the pyridine nitrogens is now completely blocked. The inclusion of APA in a second α-CD causes k_f to drop to zero because both pyridine nitrogens are now blocked and the formation reaction cannot occur.

The inclusion of the $[Fe(CN)_5(pyRpy)]^{3-}$ complex in cyclodextrin results in a bathochromic shift of the MLCT transition in the visible spectrum. Similar shifts, but of a lower magnitude, have been observed previously for the cyclodextrin inclusions of pentacyanoferrate(II)[24,27] and pentaammineruthenium(II)[28] complexes with substituted pyridine ligands. Pentacyano(N-heterocycle)ferrate(II) complexes are also known to exhibit

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significant degrees of solvatochromism.[29] In our previous studies of cyclodextrin rotaxanes of the type $[(NC)_5Fe(R(CH_2)_nR)Fe(CN)_5]^{4-}$ (R = 4,4′-bipyridine, pyrazine, or 3- or 4-cyanopyridine, $n = 8-12$), there were negligible shifts in the MLCT bands upon rotaxane formation because the cyclodextrin resided over the polymethylene chain rather than the aromatic N-heterocyclic headgroups. In the present systems the coordinated aromatic N-heterocyclic ligands reside partially or substantially inside the cyclodextrin cavity. As a result, the MLCT bands exhibit shifts similar to those exhibited in mixed aqueous/organic solvent systems. With the notable exception of those complexes containing APA, all of the complexes showed larger bathochromic shifts upon inclusion in α-cyclodextrin than in *β*-cyclodextrin. The smaller cavity size of α-cyclodextrin results in a greater degree of interaction with the ligand and, as a result, a larger bathochromic shift in the MLCT band than observed with *β*-cyclodextrin. In the case of APA the cavity of α-cyclodextrin is too small to fit over the methyl groups in the center of the ligand. Therefore, with the monomer $[(Fe(CN)_5APA]^{3-}$, the α-CD includes the uncomplexed pyridine ring. The lack of a shift in the MLCT band for the dimer is consistent with the methyl groups preventing rotaxane formation.

The decreases observed in the ligand dissociation rate constant (k_d) upon cyclodextrin inclusion of the coordinated ligands (Table 1) are similar to those exhibited by the formation rate constants, with larger decreases for the ligands (with the exception of APA) upon inclusion in α-CD compared with *β*-CD. This difference is again a result of the tighter fit of the coordinated ligand in α-CD because of its smaller cavity size. The decreases in the dissociation rate constants, which have been observed previously for other pentacyanoferrate(II) complexes containing substituted pyridine ligands,[24] are attributed primarily to the strengthening of the Fe−N bond that occurs upon inclusion in cyclodextrin. In these studies, the rate decrease was generally accompanied by a decrease in the energy of the MLCT band, attributed to a stabilization of the ground state caused by greater *π*-back-bonding from the metal to the included ligand. No effect was observed on the ligand dissociation rate constant for the $[Fe(CN)_5APA]^{3-}$ complex upon addition of α-cyclodextrin. This was not unexpected because the α-CD binds the uncomplexed pyridine such that the complexed pyridine at the opposite end of the molecule feels little effect and its ligand dissociation rate constant (Table 1) and MLCT band remain essentially unchanged.

We have observed that there is a relationship between the magnitude of the bathochromic shift of the MLCT band energy (ΔE) and the extent of the change in the ligand dissociation rate constant $\log(k_d/k_d^{CD})$ upon inclusion of the coordinated ligand in the α-cyclodextrin cavity (Figure 4). A similar relationship is observed for *β*-cyclodextrin. The relationship appears to hold for a wide range of pentacyanoferrate(II) complexes containing bis(4-pyridine) and 4-substituted pyridine ligands, and a detailed study of this correlation is in progress.

The inclusion stability constants K_{ML}^{CD} for the formation of the semirotaxane $[Fe(CN)_5\{L\cdot CD\}]^{3-}$ exhibits the trends AZP > PCA > BPE for α-cyclodextrin and APA > BPE > PCA > AZP for *β*-cyclodextrin. As with the stability constants for the free ligands, larger variations between the K_{ML}^{CD} values for the coordinated ligands were observed on inclusion in α-CD (70−1300 M^{-1}) as opposed to *β*-CD (140−800 M^{-1}), consistent with the smaller cavity size of the α-cyclodextrin.

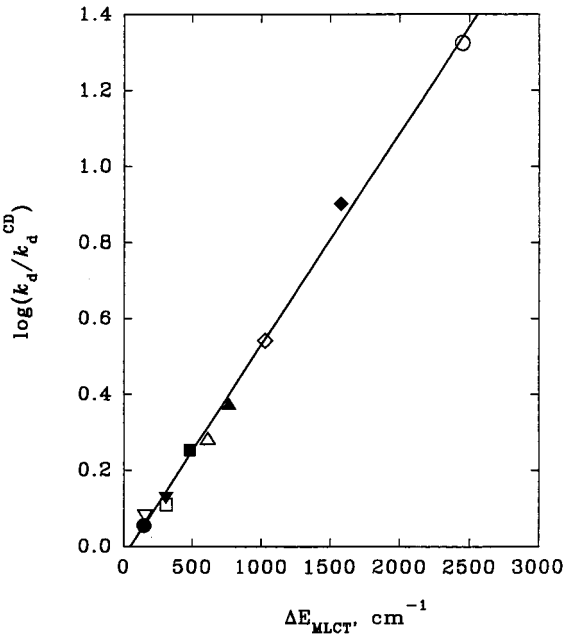

Figure 4. Plot of $\log(k_d/k_d^{CD})$ against ΔE (the shift in the energy of the MLCT band upon inclusion in α-cyclodextrin) for a variety of $[Fe(CN)_5L]^{3-}$ complexes. The ligands L are (●) 4-benzylpyridine, (▽) 4-*tert*-butylpyridine, (▼) 4-isopropylpyridine, (□) 4,4′-bipyridine, (■) 4-phenylpyridine, (△) 4-ethylpyridine, (▲) 4-picoline, (◇) PCA, (◆) BPE, and (○) AZP.

The self-assembly of the cyclodextrin rotaxane, $[(NC)_5Fe\{pyRpy\cdot CD\}Fe(CN)_5]^{6-}$ (Scheme 1), may be monitored by visible and ^1H NMR spectroscopy. The chemical shift differences for the resonances of the asymmetric H2 and H3 protons, arising from the self-assembly of the rotaxanes, are presented in Table 2. All of the ligands show larger separations between the doublets for the H-3 proton resonances compared with the H-2 proton resonances for self-assembly with α-cyclodextrin. No such trend is exhibited for self-assembly with *β*-cyclodextrin. As seen in Figure 2, the inclusion of BPE in cyclodextrin has an interesting effect on the bridge −CH═ proton resonance. Inclusion in cyclodextrin causes the two protons to be in different chemical environments, and as a result, they couple and split each other into a pair of doublets, thus confirming that self-assembly is taking place.

The stability constants K_{ML}^{CD} determined from the self-assembly studies (Table 2) were similar to those calculated by the dissociation kinetics and ^1H NMR titrations (Table 1). The limiting rate constants for the self-assembly process were the same for both α- and *β*-cyclodextrin (Table 2) and were comparable to the limiting rate constants for the dissociation of $[Fe(CN)_5]^{3-}$ from the uncomplexed ligand (Table 1). This confirms that the rate-determining step in the self-assembly process is the loss of $[Fe(CN)_5]^{3-}$ from the dimer complex.

The presence of conjugated bridging ligands between the iron(II) centers in the cyclodextrin [2]rotaxanes in this study would allow for the formation of mixed valence complexes, $[(NC)_5Fe\{L\cdot CD\}Fe(CN)_5]^{5-}$, in which the two metal centers are in nonequivalent environments.[30] Rather than having a delocalized electron, the electron may exhibit a preference for the iron center located near either the narrow or the wide rim of the cyclodextrin. Hupp and co-workers[31] have demonstrated that selective encapsulation of the pentaammineruthenium(III) center in the

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mixed-valence complex $[(NH_3)_5Ru(4,4'\text{-bipyridine})Ru(NH_3)_5]^{5+}$ by crown ethers significantly changes the energy of the intervalence metal-to-metal charge-transfer band. Examinations of the intervalence charge transfer in the near-infrared region and the nature of the waves in the cyclic voltammographs may provide evidence for the extent of the localization of the unpaired electron in the present rotaxane system. Studies of the properties of these mixed-valent cyclodextrin rotaxanes, with pentacyanoferrate and pentaaminеruthenium stoppers, are in progress.

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