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### The self-assembly of $\alpha$ -cyclodextrin rotaxanes of $\mu$ -(1,1''-( $\alpha,\omega$ -alkanediy1)bis-(4,4'-bipyridinium))bis[pentacyanoferrate-(II)] complexes

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# The self-assembly of $\alpha$ -cyclodextrin rotaxanes of $\mu$ -(1,1''-( $\alpha,\omega$ -alkanediyl)bis-(4,4'-bipyridinium))bis[pentacyanoferrate-(II)] complexes

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**Keywords:**  $\alpha$ -Cyclodextrin, rotaxanes, self-assembly, pentacyanoferrate-(II) complexes.

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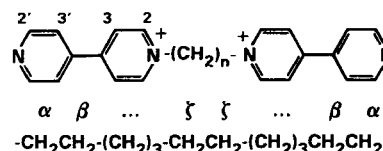
The rapid, quantitative complexation reactions of labile  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ions with  $\alpha$ -cyclodextrin ( $\alpha$ -CD) threaded 1,1''-( $\alpha,\omega$ -alkanediyl)-bis(4,4'-bipyridinium) dicationic ligands yield stable, self-assembled metal rotaxane complexes,  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}\alpha\text{-CD}\{\text{Fe}(\text{CN})_5\}]^{4-}$  ( $n=8-12$ ), in aqueous solution. The  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}\alpha\text{-CD}\}^{2+}$  inclusion complexes and the metal rotaxanes have been characterized by their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, which display pairs of proton and carbon resonances for symmetry-related nuclei upon inclusion in the asymmetric  $\alpha$ -CD cavity. The stability constants and the associated thermodynamic parameters for the  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}\alpha\text{-CD}\}^{2+}$  inclusion complexes have been determined by  $^1\text{H}$  NMR. The kinetics of the ligand substitution processes involved in the self-assembly of the metal rotaxane complexes from  $\alpha$ -CD and  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}\text{Fe}(\text{CN})_5]^{4-}$  have been measured using visible and  $^1\text{H}$  NMR spectroscopy. The kinetic and activation parameters are consistent with a rate-limiting dissociation of a  $[\text{Fe}(\text{CN})_5]^{3-}$  unit, which subsequently recomplexes with the semirotaxane species,  $[\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}\alpha\text{-CD}\{\text{Fe}(\text{CN})_5\}]^-$ , to yield the rotaxane.

## INTRODUCTION

Rotaxanes are chemical species in which a cyclic molecular bead is threaded by a linear chain bearing bulky end units, which prevent the complex from dissociating into its cyclic and linear molecular components.<sup>1</sup> There has been considerable recent interest in use of cyclodextrins, a family of cyclic oligosaccharides normally consisting of six ( $\alpha$ -CD), seven ( $\beta$ -CD), or eight ( $\gamma$ -CD)  $\alpha$ -(1 $\rightarrow$ 4)-linked D-(+)-glucopyranose units, as the cyclic components in the assemblage of rotaxane complexes.<sup>2-13</sup> Several examples of symmetrical rotaxanes based on the  $\alpha$ -cyclodextrin, threaded by alkyl chains bearing aromatic N-heterocycle,<sup>3-5</sup> carboxylate,<sup>6</sup> or cobalt amine<sup>7,8</sup> end groups, have been reported. Rao and

Lawrence<sup>9</sup> have reported a high-yield synthesis of a rotaxane in which a  $\text{dm}\beta$ -CD ( $\text{dm}\beta$ -CD = heptakis-(2,6,-*O*-dimethyl)- $\beta$ -cyclodextrin) is threaded by a dicationic chain, 3,3'-(4,4'-biphenyldiyl)bis(propylammonium), which is in turn held in the cavity through ion pairing to tetraphenylborate anions on either end. The preparation of an asymmetrical zwitterionic  $\alpha$ -CD rotaxane, bearing dimethyl(ferrocenylmethyl)ammonium and naphthalene-2-sulphonate end units, has recently been described.<sup>10</sup> Organic polyrotaxanes of  $\alpha$ -cyclodextrin have recently been reported in which 20–40 cyclodextrins are strung on poly(iminooligomethylene)<sup>11</sup> or poly(ethylene glycol) bisamine chains,<sup>13</sup> and trapped by blocking (with nicotinoyl groups) or capping (with 2,4-dinitrobenzene groups) the chains, respectively. Stoddart and co-workers have reported elegant strategies for the self-assembly of rotaxanes employing a tetracationic cyclophane as the bead, polyether threads, and triisopropylsilyl end units.<sup>14</sup>

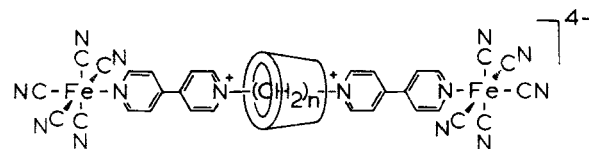
The preparations of the metal rotaxane complexes have generally involved the reaction of a semirotaxane (bearing one end unit) with a second metal complex or organic end unit. In the course of our studies into the  $\alpha$ -cyclodextrin inclusions of 1,1''-( $\alpha,\omega$ -alkanediyl)-bis(4,4'-bipyridinium) dications ( $[\{\text{bpy}(\text{CH}_2)_n\text{bpy}\}]^{2+}$ , where  $n=8-12$ ),



we observed that stable rotaxanes could be prepared rapidly and quantitatively by means of ligand substitution reactions of labile  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ions

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with the pre-threaded bridging ligands. In this paper we report the results of kinetic and spectroscopic investigations of the mechanism of the self-assembly of a series of stable  $\alpha$ -cyclodextrin rotaxanes,  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^{4-}$ .

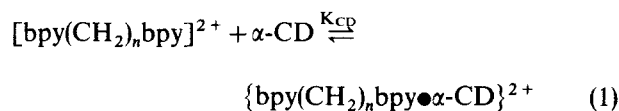


The stability constants for the  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}^{2+}$  inclusion complexes have been determined by means of  $^1\text{H}$  NMR titrations, and the kinetics of the formation and dissociation of the semirotaxane  $[\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^-$  have been measured. A preliminary account of this work has appeared.<sup>15</sup>

## RESULTS AND DISCUSSION

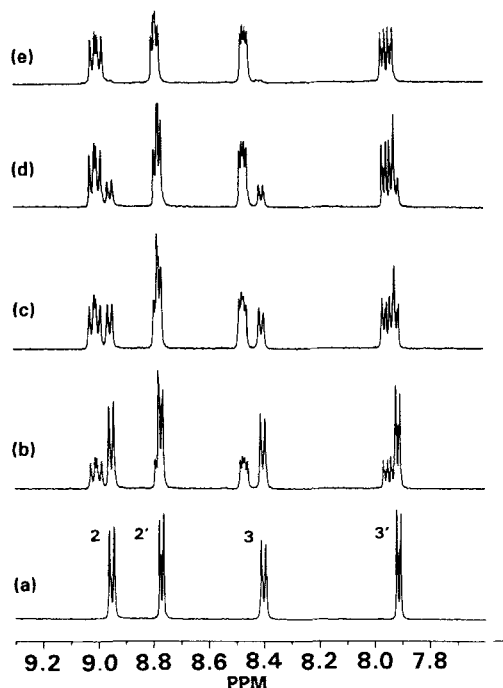
### $\alpha$ -Cyclodextrin inclusions of $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$ ligands

The  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]\text{Br}_2$  bridging ligands form stable inclusion complexes with  $\alpha$ -cyclodextrin by threading the 4,4'-bipyridinium group through the  $\alpha$ -CD cavity such that the hydrophobic alkyl chain resides within the cavity and the cationic bipyridinium end groups extend from either end.

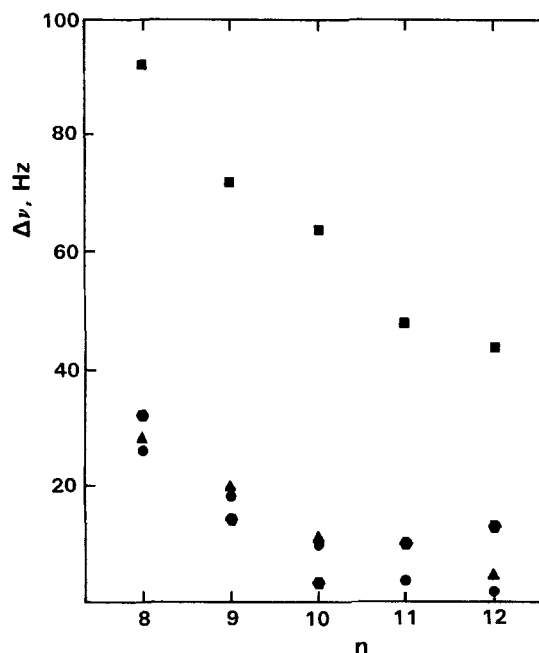


The symmetry-related  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  proton resonances in the  $^1\text{H}$  NMR spectrum of the free ligand (Fig 1(a)) are split into two sets of peaks upon formation of the inclusion complex (Fig 1(b–e)) through additions of  $\alpha$ -cyclodextrin. This splitting of the resonances (in addition to induced chemical shifts, as seen for the majority of rapidly exchanging inclusion complexes) results from the asymmetry in the  $\alpha$ -CD cavity, and the slow inclusion and release of the ligand eqn. (1) on the NMR timescale. The magnitudes of the chemical shift difference ( $\Delta\nu$ ) between the related resonances decreases as the chain length is increased (Fig 2). Similar splittings of the ligand resonances are observed in the  $^{13}\text{C}$  NMR spectra upon  $\alpha$ -CD inclusion.

The stability constants for the  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}^{2+}$  inclusion complexes were determined in aqueous solution (0.10 M NaCl) at 25 °C by means of titrations of the dicationic ligands with  $\alpha$ -cyclodextrin. The fractions of the free and included ligand were determined through integrations of the H-3', H-3, H-2,



**Figure 1** The effects of  $\alpha$ -cyclodextrin inclusion on the aromatic portion of the  $^1\text{H}$  NMR spectrum ( $\text{D}_2\text{O}$  containing 0.10 M NaCl) of  $[\text{bpy}(\text{CH}_2)_{10}\text{bpy}]^{2+}$  (4.04 mM) with  $\alpha$ -CD concentrations of (a) 0 mM, (b) 2.10 mM, (c) 4.02 mM, (d) 5.76 mM, and (e) 14.9 mM.



**Figure 2** Dependence of  $\Delta\nu$ , the chemical shift difference between the resonances for the symmetry-related guest protons; (■) H- $\beta$ , (○) H-2, (●) H-3, and (▲) H-3', on the alkyl chain length ( $n$ ) of the inclusion complex,  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}^{2+}$ .

and H- $\beta$  resonances and the titrations curves for  $n=8$ , 10, and 11 are presented in Fig 3. The calculated values of  $K_{\text{CD}}$  are presented in Table 1, along with the reported stability constants for the analogous

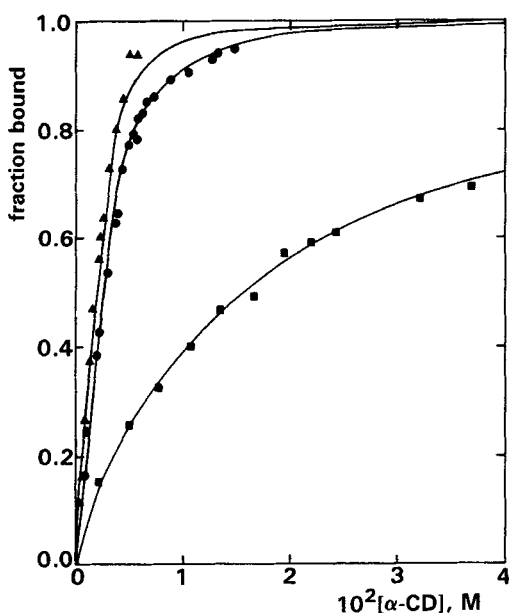
**Table 1** Stability constants for the  $\alpha$ -cyclodextrin inclusion complexes of the  $[\text{R}(\text{CH}_2)_n\text{R}]^{2+}$  guest molecules in aqueous solution, determined by  $^1\text{H}$  NMR titrations

$n$		$K_{\text{CD}}, \text{M}^{-1}$		
		$\text{R} = \text{bpy}^{+a}$	$\text{R} = \text{pyr}^{+b}$	$\text{R} = \text{COO}^{-c}$
$n = 8$		$72 \pm 2$	110	310
	$\Delta H^\circ =$	$-40 \pm 3 \text{ kJ mol}^{-1}$		$-14.9 \text{ kJ mol}^{-1}$
	$\Delta S^\circ =$	$-98 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$		$-1 \text{ J K}^{-1} \text{ mol}^{-1}$
$n = 9$		$440 \pm 30$	640	630
	$\Delta H^\circ =$	$-35 \pm 2 \text{ kJ mol}^{-1}$		$-22.6 \text{ kJ mol}^{-1}$
	$\Delta S^\circ =$	$-68 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$		$-21 \text{ J K}^{-1} \text{ mol}^{-1}$
$n = 10$		$1500 \pm 100$	2200	1400
	$\Delta H^\circ =$	$-35 \pm 3 \text{ kJ mol}^{-1}$		$-18.2 \text{ kJ mol}^{-1}$
	$\Delta S^\circ =$	$-58 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$		$0 \text{ J K}^{-1} \text{ mol}^{-1}$
$n = 11$		$3400 \pm 400$		1500
	$\Delta H^\circ =$	$-36 \pm 3 \text{ kJ mol}^{-1}$		$-25.1 \text{ kJ mol}^{-1}$
	$\Delta S^\circ =$	$-55 \pm 9 \text{ J K}^{-1} \text{ mol}^{-1}$		$-22 \text{ J K}^{-1} \text{ mol}^{-1}$
$n = 12$		$3700 \pm 500$	4800	5400
	$\Delta H^\circ =$	$-35 \pm 4 \text{ kJ mol}^{-1}$		$-25.7 \text{ kJ mol}^{-1}$
	$\Delta S^\circ =$	$-50 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$		$-14 \text{ J K}^{-1} \text{ mol}^{-1}$

<sup>a</sup> This work, in  $\text{D}_2\text{O}$  (0.10 M NaCl) at 25 °C.

<sup>b</sup> Reference 4, in  $\text{D}_2\text{O}$  at 5 °C.

<sup>c</sup> Reference 6, in  $\text{D}_2\text{O}$  (0.10 M NaOD) at 30 °C.



**Figure 3** The extent of the  $\alpha$ -cyclodextrin inclusions of the  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  ligands; (■)  $n = 8$  (3.66 mM), (●)  $n = 10$  (3.98 mM), and (▲)  $n = 11$  (3.08 mM), as a function of  $[\alpha\text{-CD}]$ , as determined by  $^1\text{H}$  NMR spectroscopy at 25 °C in  $\text{D}_2\text{O}$  containing 0.10 M NaCl.

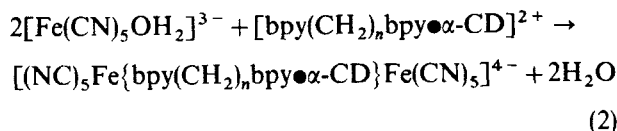
inclusion complexes with the  $[\text{pyr}(\text{CH}_2)_n\text{pyr}]^{2+}$  ( $\text{pyr} = 4\text{-pyridinium}$ )<sup>4</sup> and  $[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2]^{2-6}$  guest molecules, reported previously. The magnitudes of and the trends in  $K_{\text{CD}}$  for the three sets of related guests are similar, with the stability constant increasing with the number of methylene groups in the alkane chain. The thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  associated with  $K_{\text{CD}}$  were determined from the temperature dependence of the stability constant over the range of

4–45 °C (the upper limit determined by the onset of the signal coalescence) and are presented in Table 1. While the enthalpy and entropy parameters are both more negative than for the corresponding  $[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2]^{2-}$  inclusions,<sup>6</sup> they are similar to the values reported for the  $\alpha$ -CD complexes with the asymmetrical guests  $[\text{CA}(\text{CH}_2)_n\text{V}]^{2+}$  ( $\text{CA} = 9\text{-carbazole}$ ,  $\text{V} = 1\text{-propyl-4,4'-bipyridinium}$ , and  $n = 8, 10, \text{ and } 12$ ),  $\Delta H^\circ = -54$  to  $-57 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ = -96$  to  $-115 \text{ J K}^{-1} \text{ mol}^{-1}$ .<sup>5</sup> The negative  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters have been attributed to a greater importance of van der Waals interactions between the cavity of  $\alpha$ -CD and the methylene chain over hydrophobic effects.<sup>6,16</sup>

Above 50 °C coalescence of the resonances for the symmetry-related protons on the ligand begins. The coalescence temperatures for the  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  ligands ( $n = 9\text{--}12$ ) are in the range of 70–80 °C, increasing slightly with an increase in  $n$ , and are similar to those reported previously for the  $[\text{pyr}(\text{CH}_2)_n\text{pyr}]^{2+}$  guests.<sup>4</sup> A more precise determination of  $T_c$  is hindered by the presence of significant amounts of the free ligand present at the higher temperatures.

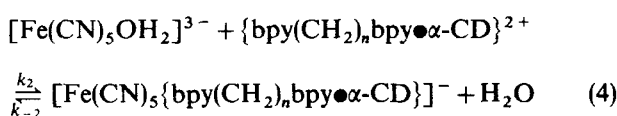
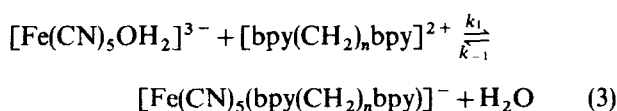
#### Formation of metal rotaxanes of $\alpha$ -cyclodextrin

The low-spin  $d^6$  pentacyanoferrate(II) group, which has a very strong affinity for aromatic N-heterocyclic ligands,<sup>17,18</sup> may be introduced as the bulky end units to form a metal rotaxane by means of a rapid ligand substitution reaction of the inclusion complex  $\{\text{bpy}(\text{CH}_2)_n\text{bpy} \bullet \alpha\text{-CD}\}^{2+}$  with the two equivalents of the  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ion (generated by rapid aquation of  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$  in solution).<sup>17</sup>

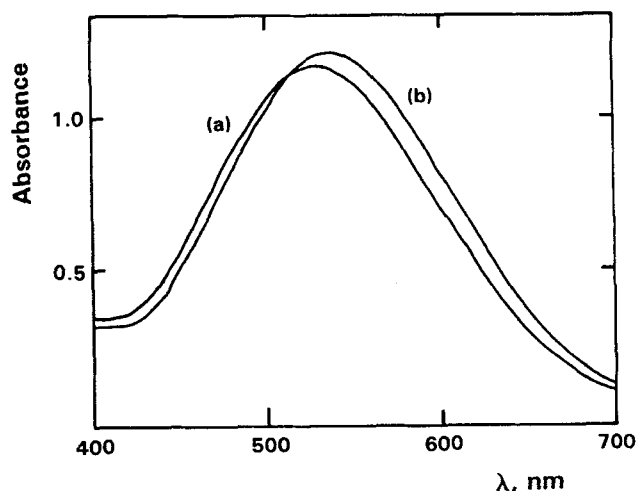


Coordination of the pentacyanoferrate(II) ions to the free or  $\alpha$ -CD included forms of the ligand results in the formation of an intense metal-to-ligand (MLCT) transition in the visible spectrum (Fig 4). The energy of the MLCT band for the rotaxane (e.g.  $\lambda_{\text{max}} = 540$  nm,  $\epsilon = 1.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for  $n = 9$ ) is found to be lower than for the bridged iron dimer complex ( $\lambda_{\text{max}} = 528$  nm,  $\epsilon = 1.10 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). We have previously observed similar bathochromic shifts accompanying cyclodextrin inclusions of coordinated ligands on pentacyanoferrate-(II) complexes containing neutral aromatic N-heterocycles and N-adamantanylpyrazinium cations.<sup>18</sup> The coordination of the pyridine nitrogens to the pentacyanoferrate (II) groups result in downfield  $^1\text{H}$  NMR chemical shifts of the ortho pyridine protons and upfield shifts in the meta protons.<sup>16</sup> The  $^1\text{H}$  NMR spectrum of the rotaxane (Fig 5) again exhibits two sets of ligand proton peaks indicating that the complexed ligand is also included in the  $\alpha$ -CD cavity.<sup>12</sup>

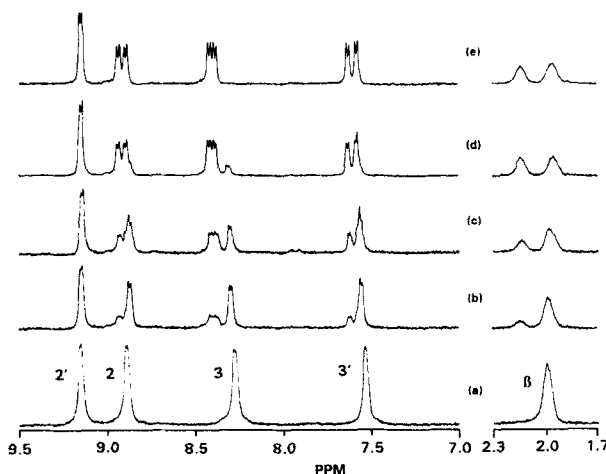
The kinetics of the formation of, and ligand dissociation from, the semirotaxane complex  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_{10}\text{bpy}\alpha\text{-CD}\}]^-$  were measured as a function of the concentration of  $\alpha$ -cyclodextrin. The reactions of the  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ion with cationic N-heterocyclic ligands proceed through a dissociative mechanism.<sup>18–20</sup>



For  $n = 10$ , the rate constant for the formation of the semirotaxane in absence of  $\alpha$ -CD,  $k_1$ , is  $7300 \pm 220 \text{ M}^{-1} \text{ s}^{-1}$  at  $25.0^\circ\text{C}$ . Upon  $\alpha$ -CD inclusion of the  $[\text{bpy}(\text{CH}_2)_{10}\text{bpy}]^{2+}$  ligand, the rate constant decreases to a limiting formation rate constant of  $k_2 = 3000 \pm 300 \text{ M}^{-1} \text{ s}^{-1}$ , close to the value of  $2800 \pm 100 \text{ M}^{-1} \text{ s}^{-1}$  measured for the reaction of the  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ion with the 1-methyl-4,4'-bipyridinium cation.<sup>19</sup> The magnitude of the observed formation rate constants depended on whether the  $\alpha$ -CD was present in the metal or ligand solutions before mixing, with the rate constants measured with the  $\alpha$ -CD in the ligand solution being 15–20% lower than when the  $\alpha$ -CD was originally in the metal complex solution. This may be attributed to a competition between the rate of ligand inclusion and the rate of ligand substitution.

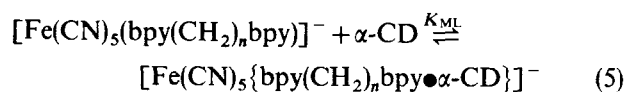


**Figure 4** The visible spectra of (a)  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_9\text{bpy})\text{Fe}(\text{CN})_5]^{4-}$  (0.87 mM) and (b)  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_9\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^{4-}$ , 45 minutes after the addition of  $\alpha$ -CD (5.0 mM) to (a).



**Figure 5** Changes in the  $^1\text{H}$  NMR spectrum of  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_9\text{bpy})\text{Fe}(\text{CN})_5]^{4-}$  (spectrum a) in the course of the self-assembly of the  $\alpha$ -cyclodextrin rotaxane complex  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_9\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^{4-}$ ; (b) 2 min, (c) 5 min, (d) 10 min, and (e) 45 min after the addition of a five-fold excess of  $\alpha$ -CD at  $295 \text{ K}$ .

The kinetics of the dissociation of the  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  ligand from the  $[\text{Fe}(\text{CN})_5(\text{bpy}(\text{CH}_2)_n\text{bpy})]^-$  complexes were measured in the presence of 0.20 M dimethylsulfoxide, which forms an inert  $[\text{Fe}(\text{CN})_5(\text{DMSO})]^{3-}$  complex upon loss of the dicationic ligand. Rate constants ( $k_{-1}$ ) of  $(3.30 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$  and  $(2.60 \pm 0.05) \times 10^{-3} \text{ s}^{-1}$  were determined for  $n = 8$  and 10, respectively, at  $25.0^\circ\text{C}$ . The rate constants decrease upon  $\alpha$ -CD inclusion of the coordinated  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  on the metal complex, and the analyses of the  $[\alpha\text{-CD}]$  dependences,



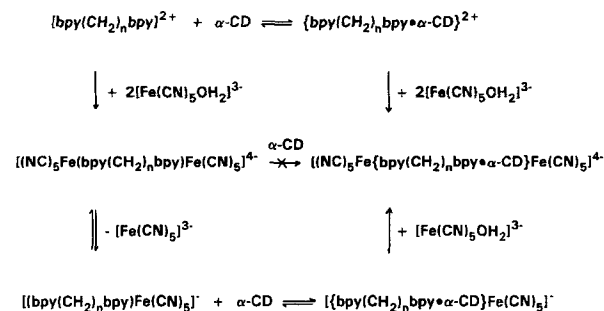
$$k_{\text{obs}} = \frac{k_{-1} + k_{-2}K_{\text{ML}}[\alpha\text{-CD}]}{1 + K_{\text{ML}}[\alpha\text{-CD}]} \quad (6)$$

yielded limiting rate constants,  $k_{-2}$ , and inclusion stability constants,  $K_{ML}$ , of  $(1.8 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$  and  $83 \pm 20 \text{ M}^{-1}$  for  $n=8$ , and  $(1.5 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$  and  $1400 \pm 200 \text{ M}^{-1}$  for  $n=10$ . The stability constants  $K_{ML}$  for the  $[\text{Fe}(\text{CN})_5\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}]^-$  semirotaxane are very similar to the values of  $K_{CD}$  for  $\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}^{2+}$  of the same methylene chain length (Table 1). The placement of a  $[\text{Fe}(\text{CN})_5]^{3-}$  unit on one end of the dicationic ligand should statistically reduce the rate of both the threading and dethreading processes by a factor of two.

### Rotaxane self-assembly

The  $\alpha$ -cyclodextrin rotaxane complexes  $[(\text{NC})_5\text{Fe}\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^{4-}$  also form spontaneously upon the addition of excess  $\alpha$ -CD to a solution containing the bridged dimer,  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_n\text{bpy})\text{Fe}(\text{CN})_5]^{4-}$ . While the pentacyanoferrate(II) end groups are too bulky to allow for direct inclusion of the iron dimer, a relatively slow dissociation of a  $[\text{Fe}(\text{CN})_5]^{3-}$  moiety, followed by the formation of the semirotaxane  $[\{\text{bpy}(\text{CH}_2)_n\text{bpy}\alpha\text{-CD}\}\text{Fe}(\text{CN})_5]^-$  and then rapid recomplexation by  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  will yield the rotaxane (Scheme I).

Scheme I



The conversion of the dimer to the rotaxane by this route may be monitored by  $^1\text{H}$  NMR (Fig 5), by observing the separation into pairs of the symmetry-related proton resonances for the  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  chain as it is included and recomplexed. It is more convenient to measure the kinetics of this process by means of visible spectroscopy. The MLCT band for the bridged iron dimer displays a bathochromic shift from 528 nm to 540 nm, with a slight increase in the molar absorptivity coefficient on formation of the rotaxane complex. A rate constant of  $3.97 \times 10^{-3} \text{ s}^{-1}$  was measured at  $25.3^\circ\text{C}$  for the self-assembly reaction ( $[\alpha\text{-CD}] = 4.1 \times 10^{-2} \text{ M}$ ,  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_9\text{bpy})\text{Fe}(\text{CN})_5]^{4-} = 2.2 \times 10^{-3} \text{ M}$ ,  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-} = 2.4 \times 10^{-3} \text{ M}$ ) of the rotaxane complex where  $n=9$ .

The magnitude of the rate constant and the corresponding activation parameters,  $\Delta H^\ddagger = 108 \pm 8 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 70 \pm 23 \text{ J K}^{-1} \text{ mol}^{-1}$ , are consistent with a dissociative ligand substitution mechanism in which the dissociation of a  $[\text{Fe}(\text{CN})_5]^{3-}$  unit from  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_n\text{bpy})\text{Fe}(\text{CN})_5]^{4-}$  is the rate-determining step. Similar dissociation rate constants ( $2\text{--}4 \times 10^{-3} \text{ s}^{-1}$ ) and activation parameters ( $\Delta H^\ddagger = 100\text{--}115 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 50\text{--}80 \text{ J K}^{-1} \text{ mol}^{-1}$ ) have also been determined for these complexes with  $n=1\text{--}8$  methylene units.<sup>20</sup>

The self-assembly of the metal rotaxane complex will occur, therefore, irrespective of the order of the addition of the  $\alpha$ -CD, bridging ligand, and  $[\text{Fe}(\text{CN})_5]^{3-}$  components. We are currently preparing bridging ligands in which one or both of the 4,4'-bipyridinium groups are substituted by pyrazinium units, to yield the asymmetrical  $\text{pyz}(\text{CH}_2)_n\text{bpy}^{2+}$  and symmetrical  $\text{pyz}(\text{CH}_2)_n\text{pyz}^{2+}$  species. The asymmetrical ligands will be employed in  $^1\text{H}$  NMR studies of the inclusion stability constants and the preference, if any, of the orientation of the ligand in the cavity. Preliminary studies with the symmetrical  $\text{pyz}(\text{CH}_2)_n\text{pyz}^{2+}$  ligands indicate that rotaxane self-assembly from the dimeric iron complex is much slower in this case, consistent with the much more inert iron-pyrazine bond.

## EXPERIMENTAL SECTION

### Materials

The  $\alpha$ -cyclodextrin (Aldrich) was dried at  $80^\circ\text{C}$  for 12 hours prior to use. Sodium aminopentacyanoferrate(II) hydrate,  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \cdot 3\text{H}_2\text{O}$ , was prepared by a reported method<sup>21</sup> and recrystallized from concentrated ammonia/methanol solutions. The  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ion was generated in solution by the rapid aqution of the ammine salt, and kept at low concentrations ( $< 10^{-4} \text{ M}$ ) to minimize dimerization processes.

The 1,1'-( $\alpha,\omega$ -alkanediyl)bis(4,4'-bipyridinium)-bromide salts,  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]\text{Br}_2 \cdot x\text{H}_2\text{O}$  ( $n=8\text{--}12$ ) were prepared by the reactions of the appropriate  $\alpha,\omega$ -dibromoalkanes (Aldrich) with 4,4'-bipyridine (Aldrich) in dimethylformamide (DMF) in a method similar to that described by Attalla *et al.*<sup>22</sup> for the shorter chain analogs. The appropriate dibromoalkane (1 mmol) in 12 mL of 1:1 DMF:diethyl ether was added dropwise, over an eight hour period to a stirred solution of 4,4'-bipyridine (20 mmol) in 5 mL of DMF at  $50^\circ\text{C}$ . After a further eight hours at this temperature, the solution was cooled and 100 mL of diethyl ether was added to complete the precipitation of the product. The crude product, containing higher charged impurities, was dissolved in warm ethanol and filtered. Dropwise addition of diethyl ether precipitated the impurity first

(filtered off), followed by the desired product. After several recrystallizations, pure compounds in 60–80% yields were obtained. The compounds were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and by elemental analysis (Canadian Microanalytical Services, Delta, B.C.).

$[\text{bpy}(\text{CH}_2)_8\text{bpy}]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ . mp 140 °C. Calcd. for  $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_2\text{Br}_2$  C, 54.26; H, 5.85; N, 9.04. Found. C, 54.18; H, 5.68; N, 9.02.

$[\text{bpy}(\text{CH}_2)_9\text{bpy}]\text{Br}_2 \cdot 3\text{H}_2\text{O}$ . mp 75 °C. Calcd. for  $\text{C}_{29}\text{H}_{40}\text{N}_4\text{O}_3\text{Br}_2$  C, 53.38; H, 6.18; N, 8.59. Found. C, 53.40; H, 5.73; N, 8.50.

$[\text{bpy}(\text{CH}_2)_{10}\text{bpy}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ . mp > 245 °C (dec). Calcd. for  $\text{C}_{30}\text{H}_{37}\text{N}_4\text{O}_{0.5}\text{Br}_2$  C, 58.04; H, 6.01; N, 9.02. Found. C, 57.99; H, 5.83; N, 8.89.

$[\text{bpy}(\text{CH}_2)_{11}\text{bpy}]\text{Br}_2 \cdot \text{H}_2\text{O}$ . mp > 245 °C (dec). Calcd. for  $\text{C}_{31}\text{H}_{40}\text{N}_4\text{OBr}_2$  C, 57.77; H, 6.26; N, 8.70. Found. C, 57.89; H, 6.02; N, 8.64.

$[\text{bpy}(\text{CH}_2)_{12}\text{bpy}]\text{Br}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ . mp > 245 °C (dec). Calcd. for  $\text{C}_{32}\text{H}_{41}\text{N}_4\text{O}_{0.5}\text{Br}_2$  C, 59.17; H, 6.36; N, 8.63. Found. C, 59.25; H, 6.29; N, 8.47.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for the aromatic and aliphatic portions of the dicationic ligands are very similar to each other. The NMR spectra for the  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  ion in  $\text{D}_2\text{O}$  are as follows:  $^1\text{H}$   $\delta$  (ppm) 8.96 (d, H-2,  $J_{2,3} = 6.9$  Hz), 8.78 (d, H-2',  $J_{2',3'} = 4.6$  Hz), 8.41 (d, H-3), 7.92 (d, H-3'), 4.65 (t, H- $\alpha$ ,  $J_{\alpha,\beta} = 7.2$  Hz), 2.04 (m, H- $\beta$ ), 1.23–1.31 (m, H- $\gamma$ , H- $\delta$ , H- $\epsilon$ , and H- $\zeta$ ).  $^{13}\text{C}$   $\delta$  (ppm) 156.3 (C-4), 152.7 (C-2'), 147.4 (C-2), 145.2 (C-4'), 128.6 (C-3), 125.1 (C-3'), 64.3 (C- $\alpha$ ), 33.1 (C- $\beta$ ), 31.1 (C- $\zeta$ ), 31.0 (C- $\epsilon$ ), 30.6 (C- $\delta$ ), 27.8 (C- $\gamma$ ). The bridged dimeric  $\mu$ -(1,1''-( $\alpha,\omega$ -alkanediyl)bis-(4,4'-bipyridinium)bis[pentacyanoferrate(II)] complexes,  $[(\text{NC})_5\text{Fe}(\text{bpy}(\text{CH}_2)_n\text{bpy})\text{Fe}(\text{CN})_5]^{4-}$ , were prepared *in situ* by the addition of one equivalent of the dicationic ligand to 2.5 equivalents of the  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  ion in aqueous solution. The  $^1\text{H}$  NMR spectra for the bridged dimer complexes,  $n = 8$ –12, were similar to each other; for  $n = 12$ ,  $^1\text{H}$  NMR  $\delta$  (ppm) 9.24 (d, H-2',  $J_{2',3'} = 6.4$  Hz), 8.92 (d, H-2,  $J_{2,3} = 6.5$  Hz), 8.35 (d, H-3), 7.64 (d, H-3'), 4.63 (t, H- $\alpha$ ,  $J_{\alpha,\beta} = 6.6$  Hz), 2.00 (m, H- $\beta$ ), 1.08–1.27 (m, H- $\gamma$ , H- $\delta$ , H- $\epsilon$ , and H- $\zeta$ ).

### Methods

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 instrument, operating at 400.1 and 100.6 MHz, respectively. The residual solvent proton signal and external  $\text{CH}_3\text{OH}$  were employed as references for the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, respectively. For the stability constant determinations, 500  $\mu\text{L}$  solutions of (typically  $1$ – $3 \times 10^{-3}$  M)  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  were titrated with consecutive additions (10–100  $\mu\text{L}$ , using a 250  $\mu\text{L}$  graduated Hamilton gas-tight syringe) of a  $\alpha$ -cyclodextrin solution (100 mM) containing the

same concentration of the guest species. The solutions were thoroughly mixed and allowed to equilibrate for several minutes in the probe (298 K) before the spectrum was acquired. The kinetic measurements on rapid reactions were performed by using a TDI Model IIA stopped-flow apparatus and data acquisition system (Cantech Scientific). Pseudo-first-order conditions of excess  $[\text{bpy}(\text{CH}_2)_n\text{bpy}]^{2+}$  concentrations ( $2.5$ – $40 \times 10^{-4}$  M) over  $[\text{Fe}(\text{CN})_5\text{OH}_2]^{3-}$  concentrations ( $2$ – $5 \times 10^{-5}$  M) were employed, and plots of  $\ln(A_\infty - A_t)$  were linear for at least three half-lives. The reported pseudo-first-order rate constants were determined from the average of four replicate experiments. The slower ligand dissociation and rotaxane self-assembly reactions were followed on Cary 3 and Hewlett-Packard 8452A spectrophotometers. The reaction temperature was maintained to within 0.1 °C over the range of 10–32 °C by means of external circulating water baths.

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