Inclusion of (*N*-Adamantan-1′-ylpyrazinium)pentacyanoferrate(II) Ion in α- and β-Cyclodextrins. Effects of Inclusion on the Spectroscopic Properties and Ligand Substitution Kinetics[1]

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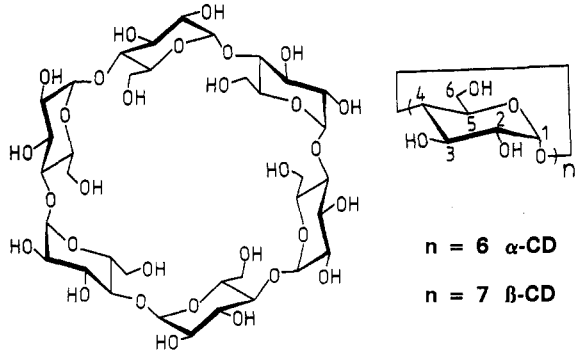
The *N*-adamantan-1′-ylpyrazinium cation ($ADpyz^+$) and the (*N*-adamantan-1′-ylpyrazinium)pentacyanoferrate(II) ion ($Fe(CN)_5(ADpyz)^{2-}$) form 1:1 inclusion complexes with α- and β-cyclodextrins (α- and β-CD) in aqueous media. The stability constants (25 °C, I = 0.10 M (NaCl), pH 6.8) for the $\{ADpyz\cdot\alpha\text{-}CD\}^+$, $\{ADpyz\cdot\beta\text{-}CD\}^+$, $Fe(CN)_5\{ADpyz\cdot\alpha\text{-}CD\}^{2-}$, and $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$ inclusion complexes were determined to be 75 ± 6, (3.1 ± 0.3) × 10^3, 72 ± 10, and (1.6 ± 0.2) × 10^3 M^{-1}, respectively, from ^1H NMR chemical shift titrations, and similar values were obtained from visible spectrophotometric titrations and ligand substitution kinetic measurements. The inclusion of the adamantyl portion of $Fe(CN)_5(ADpyz)^{2-}$ within the α- or β-CD cavity results in a bathochromic shift of the MLCT band from 658 to 672 nm. The inclusions of the free and coordinated $ADpyz^+$ ligands by the cyclodextrins have significant effects on the kinetics of the formation of $Fe(CN)_5(ADpyz)^{2-}$ from $Fe(CN)_5H_2O^{3-}$ and $ADpyz^+$, reducing k_f from 2520 ± 50 to 1110 ± 30 (α-CD) or 905 ± 40 M^{-1} s^{-1} (β-CD), and the dissociation of $ADpyz^+$ from $Fe(CN)_5(ADpyz)^{2-}$ (in the presence of 0.10 M dimethyl sulfoxide), reducing k_d from (2.07 ± 0.06) × 10^{-4} to (7.3 ± 0.3) × 10^{-5} (α-CD) or (7.6 ± 0.3) × 10^{-5} s^{-1} (β-CD). The ligand dissociation rate constants for the free $Fe(CN)_5(ADpyz)^{2-}$ complex decrease upon the addition of acetone or acetonitrile, while the values for the included complex remain unchanged in the mixed solvent solutions.

Introduction

Cyclodextrins are a class of cyclic oligosaccharide molecules normally comprised of six (α-CD), seven (β-CD), or eight (γ-CD) α-(1→4)-linked D-(+)-glucopyranose units,[2] with a toroidal hydrophobic cavity capable of including a wide variety of guest substances.[2,3] The exterior of the cyclodextrin is hydrophilic, with the both the narrow and wide rims of the cavity surrounded by hydroxyl groups.



The use of the hydroxyl oxygens on cyclodextrins as inner-sphere donor atoms for metal ions has been limited to a few examples,[4-6] including first-row transition metal species of the form $[M_2(OH)_2\beta\text{-}CD\cdot 2H_2O]^{n-}$.[4,5] There is, however, a growing interest in the use of cyclodextrins and other host molecules (e.g. crown ethers,[7] natural ionophores,[8] and calixarenes[9]) as second-sphere ligands for transition metal complexes.[10] The cyclodextrin may act as a second-coordination sphere of the metal complex by including hydrophobic organic inner-sphere ligands such as η^5-cyclopentadienyl and other arenes,[11] 1,5-cyclooctadiene,[12] trimethylphosphine,[13] and aromatic N-heterocycles.[14] Cyclodextrins may also form metal rotaxane complexes by including bridging ligands such as α,ω-diaminoalkanes and α,ω-bis(4,4′-dipyridinium)alkanes coordinated to chlorobis(ethylenediamine)cobalt(III)[15] and pentacyanoferrate(II) centers,[16] respectively.

Among the organic compounds exhibiting the strongest binding to the α- and β-cyclodextrins[17-20] and modified cyclodextrins[19d,21] are a series of substituted adamantanes. The adamantan-1-

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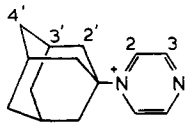
ylcarboxylic acid and its conjugate base, for example, have β-CD inclusion stability constants of 3×10^5 and 3×10^4 M^{-1}, respectively, at 25 °C in 0.10 M NaCl,[18,20] while the stability constants for the inclusion of adamantan-1-ylamine and the adamantan-1-ylammonium ion have been determined to be 1×10^5 and 8×10^3 M^{-1}, respectively.[18-20] A major reason for the strong binding within the β-CD cavity is the close match of the adamantane diameter (≈7 Å) with the diameter of the β-cyclodextrin cavity. Lower 1:1 stability constants (K_L = 100–400 dm^3 mol^{-1}) have measured for the smaller α-cyclodextrin (5.5 Å), and with the shallower fit of the adamantane guest, 2:1 host–guest complexes have also been detected for neutral substituted adamantanes. A wide variety of techniques have been employed in the detection and quantification of cyclodextrin inclusion complexes with these and other substances,[2] including UV–visible absorption, fluorescence, circular dichroism, NMR, conductivity, and acid–base titrations.

In our laboratory we have been investigating the use of UV–visible and NMR spectroscopy, along with ligand substitution kinetic measurements, to determine the nature and extent of the inclusions of neutral and cationic aromatic N-heterocyclic ligands in α- and β-cyclodextrin.[22] The pentacyanoferrate(II) center, $Fe(CN)_5^{3-}$, is employed as a kinetic and spectroscopic probe of the inclusion processes as it rapidly forms stable, highly colored, diamagnetic $Fe(CN)_5L^{(3-n)-}$ complexes with these L^{n+} ligands.[23] In the course of these investigations we have prepared the perchlorate salt of the N-adamantan-1'-ylpyrazinium cation ($ADpyz^+$) for the study of its binding to α- and β-cyclodextrin.



$ADpyz^+$

In this paper the results of spectroscopic and kinetic studies of the inclusion complexes of the $ADpyz^+$ ligand and its pentacyanoferrate(II) complex, $Fe(CN)_5(ADpyz)^{2-}$, with α- and β-cyclodextrin, are reported. The effects of inclusion of the ligand and the metal complex on the kinetics of the complex formation and ligand dissociation, respectively, have been investigated. The stability constants of the $\{ADpyz{\cdot}CD\}^+$ and $[Fe(CN)_5\{ADpyz{\cdot}CD\}]^{2-}$ guest–host complexes, determined from ^1H NMR and visible spectrophotometric titrations and from the analysis of the kinetic data, are compared with reported values for anionic and cationic substituted adamantanes. The spectroscopic and kinetic effects of cyclodextrin inclusion of the complex are related to similar effects observed for pentacyanoferrate(II) complexes in mixed solvent systems.

Experimental Section

Materials. The α- and β-cyclodextrins (Aldrich) were dried in a vacuum oven at 80 °C for 12–16 h prior to use. Sodium amminepentacyanoferrate(II) hydrate, $Na_3[Fe(CN)_5NH_3]{\cdot}3H_2O$, was prepared by a literature method[24] and recrystallized from concentrated ammonia. Dissolution of the complex in aqueous solution ($<1 \times 10^{-4}$ M) results in rapid aquation to form the $Fe(CN)_5OH_2^{3-}$ ion (λ_{max} = 444 nm, ϵ = 660 M^{-1} cm^{-1}).[25] The concentrations of the aqua complex were kept low to prevent complications from dimerization processes.

N-adamantan-1'-ylpyrazinium perchlorate was prepared by the reaction of 1-bromoadamantane and pyrazine in nitromethane in the presence of silver perchlorate, following the method reported previously for the analogous *N*-adamantan-1'-ylpyridinium perchlorate.[26] Anal. Calcd for $C_{14}H_{19}N_2ClO_4$: C, 53.41; H, 6.08; N, 8.90. Found: C, 53.11; H, 6.10; N, 8.58 (Canadian Microanalytical Services, Delta, BC). ^1H NMR (D_2O vs TSP): δ 9.43 (d, 2H, H3), 9.26 (d, 2H, H2, $J_{2,3}$ = 4.4 Hz), 2.41 (m, 3H, H3'), 2.36 (d, 6H, H2', $J_{2,3}$ = <0.5 Hz), 1.86 (d, 3H, H4a'), 1.80 (d, 3H, H4b', $J_{4a,4b}$ = 12.7 Hz). ^{13}C NMR (D_2O): δ 152.8 (C3), 136.7 (C2), 75.0 (C1'), 43.7 (C2'), 36.6 (C4'), 32.2 (C3'). *N*-Methylpyrazinium iodide was prepared by a reported procedure[27] and recrystallized from ethanol.

Physical Measurements. The UV–visible spectra and the kinetics measurements of the ligand dissociation reactions were recorded on Hewlett-Packard 8452A and Cary 3 spectrophotometers. The more rapid metal complex formation kinetic studies were performed by using a TDI Model IIA stopped-flow apparatus and data acquisition system (Cantech Scientific). The ligand substitution reactions were 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 four to six replicate experiments performed for the stopped-flow measurements and two replicate experiments for the ligand dissociation reactions (agreement in k_{obs} within 3%). The reaction temperture was maintained to within 0.1 °C over the range 10–32 °C by using external circulating water baths. The pH of the reaction solutions was maintained at 6.8 by means of a phosphate buffer and the ionic strength was kept at 0.10 M by using added sodium chloride.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400/Aspect 3000 instrument. The samples were prepared in D_2O containing 0.10 M NaCl, using TSP in a sealed capillary as an external reference, and the HOD resonance was suppressed with a 3.0-s presaturation pulse. For the stability constant determinations, 500-μL solutions of $ADpyz^+$ or $Fe(CN)_5(ADpyz)^{2-}$ ($(2–4) \times 10^{-3}$ M) were titrated with consecutive additions (10–100 μL, using a 250-μL Hamilton gastight syringe) of α- (up to 1.0×10^{-1} M) or β-CD solutions (up to 1.5×10^{-2} M) containing the same concentration of the guest species. The solutions were thoroughly mixed and allowed to equilibrate for several minutes at 298 K in the probe before the spectrum was acquired.

Cyclic voltammetric measurements were performed by using a CV1B cyclic voltammograph (Bioanalytical Systems) attached to a Houston Instruments 100 X-Y recorder. The working (Pt button) and auxiliary (Pt wire) electrodes in the sample solution were separated from the reference electrode (Ag/AgCl) by a glass frit.

Stability Constant Computations. The inclusion stability constants and estimated errors were calculated from ligand substitution kinetic data and from ^1H NMR and visible spectrophotometric titration data by the application of nonlinear least-squares and Simplex optimization programs to the equations (eq 1 and eq 3, 7, or 10) for a 1:1 guest–host model.[22,28,29] The concentration of the inclusion complex (L·CD) is related to the stability constant by eq 1, where $B = ([L]_T + [CD]_T + K^{-1})$. In

$$[L{\cdot}CD] = \frac{B - (B^2 - 4[L]_T[CD]_T)^{1/2}}{2} \quad (1)$$

this equation L refers to $ADpyz^+$ or $Fe(CN)_5(ADpyz)^{2-}$, with K representing the stability constants K_L and K_{ML} for the inclusion complexes $\{ADpyz{\cdot}CD\}^+$ and $Fe(CN)_5\{ADpyz{\cdot}CD\}^{2-}$, respectively.

Results

Inclusion Stability Constants. The stability constants, K_L, for the inclusion complexes formed between the *N*-adamantan-1'-ylpyrazinium cation and the α- and β-cyclodextrins at 25 °C were determined by means of ^1H NMR titrations in D_2O (0.10

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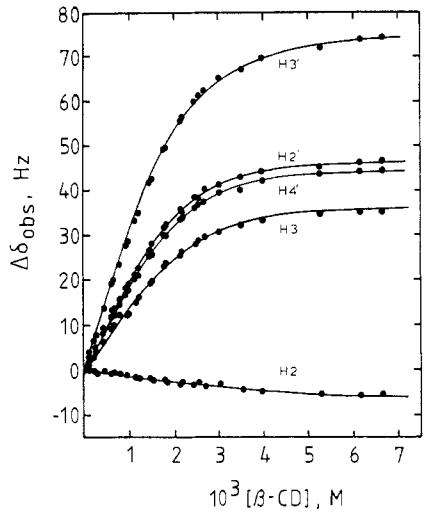

Figure 1. ^{1}H NMR chemical shifts differences for the ADpyz$^+$ protons ($\Delta(\delta_{obs})$ is the chemical shift of the included ligand minus the chemical shift of the free ligand) as a function of [β-CD] at 25 °C in D_2O (0.10 M NaCl).

M NaCl).

$$ADpyz^+ + CD \overset{K_L}{\rightleftharpoons} \{ADpyz{\cdot}CD\}^+ \quad (2)$$

The formation of the inclusion complex resulted in downfield chemical shifts of the adamantyl protons and the H3 proton on the pyrazinium ring and in upfield shifts for the interior H3 and H5 protons of the cyclodextrin as well as for the H2 proton on the pyrazinium ring (Figure 1). The observed chemical shift changes, $\Delta(\delta_{obs})$, are proportional to the fraction of the ligand that is included in the CD cavity.

$$\Delta(\delta_{obs}) = \frac{\Delta(\delta_{lim})[\{ADpyz{\cdot}CD\}^+]}{[ADpyz^+]_T} \quad (3)$$

By employment of the changes in the chemical shifts ($\Delta(\delta_{obs})$) of the adamantyl and pyrazinium H2 protons, values of 75 ± 6 and 3100 ± 330 M^{-1} were determined (eqs 1 and 3) for the stability constant K_L with α- and β-CD, respectively, at 25 °C in 0.10 M NaCl. The limiting changes in the ^{1}H and ^{13}C chemical shifts ($\Delta(\delta_{lim})$) for the ADpyz$^+$ nuclei upon formation of the β-CD inclusion complex are presented in Table I. The ^{13}C NMR chemical shift changes for the ADpyz$^+$ ligand upon inclusion in the α- and β-CD cavities are generally similar in sign and magnitude to those reported for the adamantan-1-ylammonium cation (Table I),[18c] which exhibits similar inclusion stability contants of 50 and 8000 M^{-1}, respectively.

The ligand substitution reaction between the labile Fe(CN)$_5$OH$_2^{3-}$ ion and the ADpyz$^+$ cation in aqueous solution results in the rapid formation of a stable blue complex, Fe(CN)$_5$(ADpyz)$^{2-}$, which exhibits an intense metal-to-ligand charge transfer (MLCT) band at 658 nm (ϵ = 14 000 M^{-1} cm^{-1}), of similar energy and intensity to those for other pentacyanoferrate(II) complexes of *N*-alkylpyrazinium cations.[23,30,31] There is also a much weaker d–d transition ($^1A_1 \rightarrow {}^1E(1)$) at 378 nm ($\epsilon$ = 550 M^{-1} cm^{-1}). The addition of either α- or β-cyclodextrin to a solution of the complex produces a bathochromic shift in the MLCT band to 672 nm (ϵ = 14 700 M^{-1} cm^{-1}), while the d–d transition remains virtually unchanged upon ligand inclusion.

$$Fe(CN)_5(ADpyz)^{2-} + CD \overset{K_{ML}}{\rightleftharpoons} Fe(CN)_5(\{ADpyz{\cdot}CD\})^{2-} \quad (4)$$

The stability constants K_{ML} were determined from spectrophotometric titrations of Fe(CN)$_5$(ADpyz)$^{2-}$ with α- and β-cyclodextrin, monitored at 690 and 730 nm. At 25 °C the values of K_{ML} were calculated[28] to be 86 ± 6 M^{-1} (α-CD) and 2350 ± 200 M^{-1} (β-CD). Both the free metal complex and the CD inclusion complexes display solvatochromism. The additions of 30% (by volume) of acetone and acetonitrile (higher proportions of the organic solvent result in precipitation of the metal complex and/or CD) resulted in bathochromic shifts of the MLCT transitions to the 688–692-nm range from the aqueous solution values of 658 and 672 nm for the Fe(CN)$_5$(ADpyz)$^{2-}$ and Fe(CN)$_5$\{ADpyz·CD\}$^{2-}$ species, respectively.

The ^{1}H NMR spectrum of the Fe(CN)$_5$(ADpyz)$^{2-}$ complex contains peaks at 9.75 (H3) and 8.52 (H2) ppm for the pyrazinium group, which represent downfield and upfield shifts, respectively, from the positions in the free ligand. The chemical shifts for the protons on the coordinated ADpyz$^+$, measured in 0.10 M NaCl at 25 °C, display behavior similar to that of the free ligand when included in the α- and β-CD cavities (Figure 2). The H3 proton in the metal complex shifts further downfield (+38 Hz) than

Table I. ^{1}H and ^{13}C NMR Chemical Shift Displacements ($\Delta(\delta_{lim})$) Resulting from the Inclusions of ADpyz$^+$ and Fe(CN)$_5$(ADpyz)$^{2-}$ in α- and β-Cyclodextrins

	$\Delta(\delta_{lim})$, ppm			
	ADpyz$^+$		Fe(CN)$_5$(ADpyz)$^{2-}$	
nucleus	β-CD	α-CD	β-CD	α-CD
		Adamantane		
H2′	+0.13	+0.15	+0.13	+0.13
H3′	+0.20	+0.22	+0.21	+0.20
H4′	+0.12	+0.14	+0.12	+0.13
C1′	−0.07 (−0.14)[b]	−0.22 (−0.20)[c]	−0.49	−0.60
C2′	+0.31 (+0.21)[b]	+0.29 (−0.02)[c]	+0.18	+0.07
C3′	−0.06 (−0.01)[b]	+0.14 (−0.01)[c]	−0.14	−0.04
C4′	+0.49 (+0.44)[b]	+0.80 (+0.64)[c]	+0.41	+0.68
		Pyrazine		
H2	−0.02	+0.10	−0.04	+0.03
H3	+0.10	+0.01	+0.05	−0.05
C2	−0.48	+0.04	−0.76	+0.70
C3	+0.35	+0.51	+0.41	+0.46
		Cyanides		
CN_{trans}			+0.65	
CN_{cis}			+0.86	

[a] $\Delta(\delta_{lim})$ is the chemical shift of the inclusion complex minus the chemical shift of the free ligand or metal complex. [b] Values in parentheses are for the chemical shift changes for the β-CD inclusion of the adamantan-1-ylammonium ion.[18c] [c] Values in brackets are for the chemical shift changes for the α-CD inclusion of the adamantan-1-ylammonium ion.[19c]

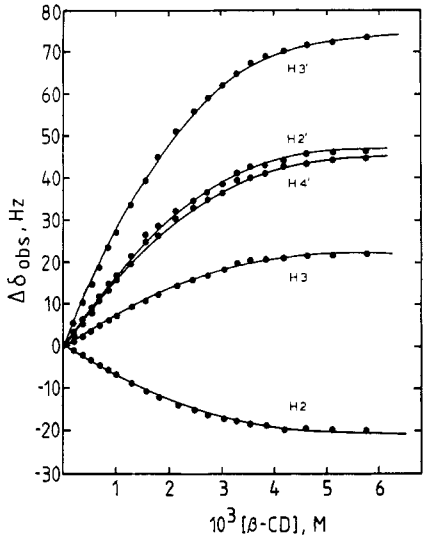

Figure 2. ^{1}H NMR chemical shifts differences for the Fe(CN)$_5$(ADpyz)$^{2-}$ protons ($\Delta(\delta_{obs})$ is the chemical shift of the included complex minus the chemical shift of the free complex) as a function of [β-CD] at 25 °C in D_2O (0.10 M NaCl).

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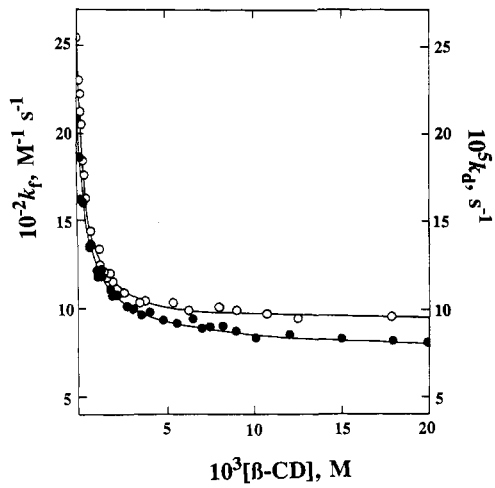

Figure 3. Dependences of the second-order rate constant k_f for the reaction of $Fe(CN)_5OH_2^{3-}$ with $ADpyz^+$ (○) and the first-order rate constant k_d for the dissociation of $ADpyz^+$ from $Fe(CN)_5(ADpyz)^{2-}$ in the presence of 0.10 M DMSO (●), on [β-CD] at 25.0 °C (I = 0.10 M (NaCl), pH 6.8).

does the same proton in the free ligand (+21 Hz), while the H2 proton shifts less upfield (–7 Hz) than in the free ligand (–21 Hz). The downfield shifts observed for the protons of the included adamantyl group are similar to those found for the free ligand inclusion. From the dependence of the displacement of adamantyl proton shifts with [CD], K_{ML} values of 72 ± 10 M^{-1} and 1590 ± 240 M^{-1} were determined (eqs 1 and 3) for α- and β-CD, respectively. The chemical shift changes of the ^1H and ^{13}C nuclei of the $Fe(CN)_5(ADpyz)^{2-}$ ion upon inclusion are presented in Table I.

Ligand Substitution Kinetics. The ligand substitution reaction of the $Fe(CN)_5OH_2^{3-}$ ion with the $ADpyz^+$ cation is a rapid process

$$Fe(CN)_5OH_2^{3-} + ADpyz^+ \xrightarrow{k_1} Fe(CN)_5(ADpyz)^{2-} \quad (5)$$

observed pseudo-first-order rate constants displaying a first-order dependence on [$ADpyz^+$]. The second-order rate constant, k_1, at 25.0 °C and an ionic strength of 0.10 M (NaCl) is (2.52 ± 0.05) × 10^3 M^{-1} s^{-1}, with $\Delta H_1^\ddagger$ = 68.9 ± 1.7 kJ mol^{-1} and $\Delta S_1^\ddagger$ = 51.2 ± 5.0 J K^{-1} mol^{-1}. Similar rate constants and activation parameters have been reported for the substitution reactions with other N-alkylpyrazinium cations under these solution conditions.[23,30,31] The rate constant for the formation of $Fe(CN)_5(ADpyz)^{2-}$ is observed to decrease as the concentration of added α- or β-cyclodextrin is increased (Figures 3 and 4).

$$Fe(CN)_5OH_2^{3-} + \{ADpyz\cdot CD\}^+ \xrightarrow{k_2} Fe(CN)_5\{ADpyz\cdot CD\}^{2-} \quad (6)$$

The observed second-order rate constants for the formation of the substituted pentacyanoferrate(II) complex may be expressed in terms of the specific rate constants k_1 and k_2, as in eq 7.

$$k_f = \frac{k_1[ADpyz^+] + k_2[\{ADpyz\cdot CD\}^+]}{[ADpyz^+]_T} \quad (7)$$

A nonlinear least-squares fit of the experimental rate constants to eqs 1 and 7, using the measured value of k_1, yields a rate constant of 905 ± 40 M^{-1} s^{-1} for k_2 and a stability constant of (3.03 ± 0.25) × 10^3 M^{-1} for the β-CD inclusion complex. The activation parameters associated with k_2, $\Delta H_2^\ddagger$ = 66.2 ± 2.3 kJ mol^{-1} and $\Delta S_2^\ddagger$ = 33.6 ± 6.7 J K^{-1} mol^{-1} were determined at a high β–CD concentration of 2.0 × 10^{-2} M. On the basis of the relatively small enthalpy of formation of the adamantan-1-ylammonium/β-CD complex, ΔH° = –27.8 ± 1.3 kJ mol^{-1}, the $ADpyz^+$ cation would be expected to be nearly completely included

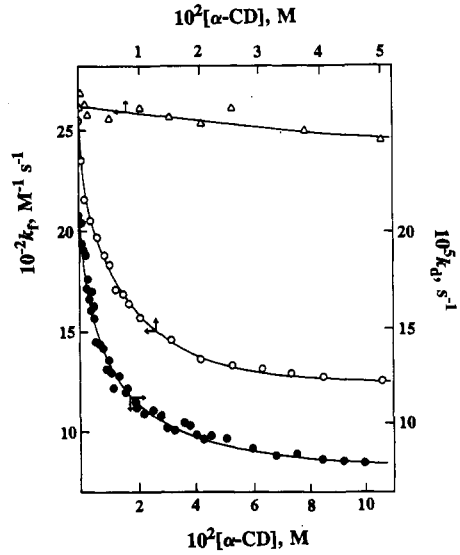

Figure 4. Dependences of the second-order rate constants k_f for the reactions of $Fe(CN)_5OH_2^{3-}$ with $ADpyz^{2+}$ (○) and N-Mepyz$^+$ (▲) and the first-order rate constant k_d for the dissociation of $ADpyz^{2+}$ from $Fe(CN)_5(ADpyz)^{2-}$ (●), on [β-CD] at 25.0 °C (I = 0.10 M (NaCl), pH 6.8).

even at the highest temperature (32 °C) used in the determination of the activation parameters.

From a fit of the experimental rate constants in the presence of added α-CD (Figure 4), values of k_2 = 1110 ± 30 M^{-1} s^{-1} and K_{ML} = 165 ± 12 M^{-1} were determined. A study of the kinetics of the reaction of $Fe(CN)_5OH_2^{3-}$ with the N-methylpyrazinium cation (Figure 4) revealed that the formation rate constant (k_1 = (2.60 ± 0.07) × 10^3 M^{-1} s^{-1}) decreased only very slightly as the concentration of α-CD was increased up to 0.05 M. This observation suggests the stability constant for a second α-CD binding to the pyrazinium end of $ADpyz^+$ is likely to be very small (< 10 M^{-1}).

The kinetics of the dissociation of the $ADpyz^+$ ligand from the $Fe(CN)_5(ADpyz)^{2-}$ may be followed by adding a large excess of another complexating ligand. Dimethyl sulfoxide (DMSO) is frequently employed in kinetics studies of the dissociation reactions of substituted pentacyanoferrate(II) complexes because it forms a very stable (k_{-DMSO} = 7.5 × 10^{-5} s^{-1} at 25 °C (I = 1.0 M ($LiClO_4$)[32]),colorless (λ_{max} = 352 nm) product, $Fe(CN)_5(DMSO)^{3-}$. Limiting first-order rate constants, k_{-1}, are observed at high DMSO concentration, and in this study the DMSO concentration was maintained at 0.10 M.

$$Fe(CN)_5(ADpyz)^{2-} + DMSO \xrightarrow{k_{-1}} Fe(CN)_5(DMSO)^{3-} + ADpyz^+ \quad (8)$$

For the reaction in equation 6, k_{-1} = (2.07 ± 0.06) ± 10^{-4} s^{-1} at 25.0 °C (I = 0.10 M(NaCl)), with $\Delta H^\ddagger$ = 109 ± 1 kJ mol^{-1} and $\Delta S^\ddagger$ = 52 ± 4 J K^{-1} mol^{-1}. The addition of either α- or β-cyclodextrin resulted in a decrease in the rate constant for dissociation of $Fe(CN)_5(ADpyz)^{2-}$ ([$Fe(CN)_5(ADpyz)^{2-}$] = 5.0 × 10^{-5} M, with a slight excess of $Fe(CN)_5OH_2^{3-}$ to ensure complete complexation of $ADpyz^+$) in the presence of 0.10 M DMSO (Figures 3 and 4).

$$Fe(CN)_5\{ADpyz\cdot CD\}^{2-} + DMSO \xrightarrow{k_{-2}} Fe(CN)_5(DMSO)^{3-} + \{ADpyz\cdot CD\}^+ \quad (9)$$

The observed rate constant for ligand dissociation may be expressed in terms of the specific rate constants k_{-1} and k_{-2}, as in eq 10. A non-linear least-squares fit of the observed dissociation rate constants to eqs 1 and 10 yielded k_2 = (7.9 ± 0.3) × 10^{-5} s^{-1} and K_{ML} = 1850 ± 110 M^{-1} in the case of β-CD and k_2 = (7.2

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

$$k_d = \frac{k_{-1}[Fe(CN)_5(ADpyz)^{2-}] + k_{-2}[Fe(CN)_5\{ADpyz\cdot CD\}^{2-}]}{[Fe(CN)_5(ADpyz)^{2-}]_T} \quad (10)$$

± 0.3) × 10^{-5} s^{-1} and K_{ML} = 137 ± 7 M^{-1} for α-CD. Using a large excess of β-CD (2.0 × 10^{-2} M), the activation parameters corresponding to the temperature dependence of k_{-2} were found to be $\Delta H_{-2}^{\ddagger}$ = 119 ± 2 kJ mol^{-1} and $\Delta S_{-2}^{\ddagger}$ = 74 ± 7 J K^{-1} mol^{-1}. Decreasing the DMSO concentration leads to only a very slight increase in k_{-2}, which is not unexpected as k_{-2} for the included $ADpyz^+$ ligand is very similar to the value for DMSO itself. A study of the effect of [β-CD] on the kinetics of dissociation of the *N*-methylpyrazinium cation ($Mepyz^+$) from $Fe(CN)_5(Mepyz)^{2-}$ at 25.0 °C (I = 0.10 M (NaCl)) revealed that k_d was independent of [β-CD] ((0–8) × 10^{-3} M), with k_{-1} = (4.47 ± 0.06) × 10^{-4} s^{-1}.

The rate constants for the dissociation of $ADpyz^+$ from the $Fe(CN)_5(ADpyz)^{2-}$ complex decrease upon additions of an organic cosolvent such as acetone or acetonitrile. Figure 5 presents the dependence of the dissociation rate constants ($\ln k_d$) on the solvent number[33] for both the $Fe(CN)_5(ADpyz)^{2-}$ and $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$ species.

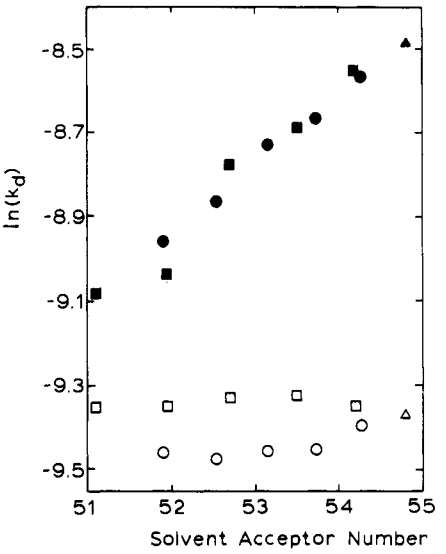

Figure 5. Plots of ln k_d against the solvent acceptor number for the dissociation of $ADpyz^+$ from $Fe(CN)_5(ADpyz)^{2-}$ in (▲) water, (■) aqueous acetone, and (●) aqueous acetonitrile and from $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$ in (△) water, (□) aqueous acetone, and (○) aqueous acetonitrile.

Table II. Cyclodextrin Inclusion Stability Constants for $\{ADpyz\cdot CD\}^+$ (K_L) and $Fe(CN)_5\{ADpyz\cdot CD\}^{2-}$ (K_{ML}) and Ligand Substitution Kinetic Parameters at 25.0 °C

parameter	α-CD	β-CD
K_L (NMR), M^{-1}	75 ± 6	3100 ± 330
K_{ML} (NMR), M^{-1}	72 ± 10	1590 ± 240
K_{ML} (UV–vis), M^{-1}	86 ± 6	2350 ± 200
K_L (kinetics), M^{-1}	165 ± 12	3030 ± 250
k_1, M^{-1} s^{-1}	2520 ± 50	2520 ± 50
k_2, M^{-1} s^{-1}	1110 ± 30	905 ± 40
K_{ML} (kinetics), M^{-1}	137 ± 7	1850 ± 110
10^4 k_{-1}, s^{-1}	2.07 ± 0.06	2.07 ± 0.06
10^4 k_{-2}, s^{-1}	0.79 ± 0.03	0.72 ± 0.03

Discussion

The stability constants determined in this study for the α- and β-cyclodextrin inclusion complexes with $ADpyz^+$ and $Fe(CN)_5(ADpyz)^{2-}$, by using ligand substitution kinetics and ^1H NMR and visible spectrophotometric titrations, are summarized in Table II. In the present work there is a reasonably good agreement in the magnitude of the stability constants among the three methods of determination. The stability constants for β-cyclodextrin inclusion complexes have been found to be somewhat dependent on the nature and concentrations of ions employed as electrolytes and buffers,[34,35] and this may account for some of the differences in the values measured by the different techniques in Table II. In the ligand dissociation kinetic studies, the presence of the 0.10 M dimethyl sulfoxide will affect the binding constant of the coordinated ligand. We have observed that the binding constants for β-CD inclusion complexes of N-heterocyclic ligands decrease somewhat in the presence of DMSO (e.g. for 4-*tert*-butylpyridine, K_L decreases from 7400 to 5300 M^{-1} in the presence of 0.20 M DMSO),[22] and this may account in part for reduced inclusion stability contant measured for the coordinated $ADpyz^+$ in the β-CD cavity.

The stability constant for the inclusion complex formed between β-cyclodextrin and the $ADpyz^+$ cation, 3100 M^{-1}, is somewhat smaller than the values reported for the adamantan-1-ylammonium and adamantan-1-ylcarboxylate ions under similar solution conditions. Hydrogen bonding between the secondary cyclodextrin hydroxyl groups and the ammonium or carboxylate substituents on the adamantanes has been suggested to enhance the stability of the inclusion complexes.[19d] The (*N*-adamantan-1′-ylpyrazinium)pentacyanoferrate(II) complex forms a strong inclusion adduct with β-CD in solution. The average of the K_{ML} values determined for $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$, 1900 M^{-1}, is the one of the higher values reported to date for an inclusion adduct of a transition metal complex with β-cyclodextrin in aqueous solution.[10,11]

From studies on several β-CD inclusion complexes with charged substituted adamantanes, Palepu and Reinsborough have concluded that the snugness of the fit of the adamantyl group in the cyclodextrin cavity is the main factor responsible for the high binding constants and that a positive or negative charge on substituents in the 1- or 2-position reduces the binding constant somewhat.[20] The spectroscopic and kinetic data in this study were fit to a model of only 1:1 binding of the $ADpyz^+$ cation and $Fe(CN)_5(ADpyz)^{2-}$ complex to β-CD. With the *N*-adamantan-1′-ylpyrazinium guest, the binding of a second β-CD to the pyrazinium moiety is unlikely as we have found that pyrazine and the pentacyanoferrate(II) ion have very low affinities for the β-CD cavity ($K_L \leq 5$ M^{-1}).[22] Microcalorimetry and methyl orange displacement studies of α-CD with the neutral adamantan-1-ylamine and adamantane-1 carboxylic acid guests reveal that 2:1 host–guest binding occurs,[18d,19b,19c] as with the smaller internal diameter of α-CD the guest molecules do not penetrate deeply into the cavity as they do with β-CD.[18] With the charged conjugate acid and base species, respectively, 2:1 binding does not occur. In the present study it is observed that $ADpyz^+$ forms a weak 1:1 complex (K_L = 80 M^{-1}) with α-CD, with no evidence for appreciable 2:1 binding.

The rate constant for the reaction between the $Fe(CN)_5OH_2^{3-}$ ion and the $ADpyz^+$ cation is observed to decrease from 2530 to 905 and 1110 M^{-1} s^{-1} upon inclusion of the entering ligand in the β- and α-cyclodextrin cavities, respectively. The ligand substitution reaction proceeds by an ion-pair dissociative (D_{IP}) mechanism in which the rate-determining step involves the dissociation of the aqua ligand from the metal center within a $[Fe(CN)_5OH_2\|ADpyz]^{2-}$ ion-pair complex.[23] The diminution of the observed second-order rate constant upon inclusion of the ligand, which we have also observed with a variety of neutral N-heterocyclic ligands,[22] is therefore related to a decrease in the proportion of effective ion-pairs which may lead to substitution (by placing the ligand in proximity to the site of the leaving aqua ligand). By inclusion of the $ADpyz^+$ ligand within the CD cavity

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the positive charge on the ligand is also less accessible to form an ion pair with the $Fe(CN)_5OH_2^{3-}$ anion. The resulting entering ligand, $\{ADpyz\cdot CD\}^+$, is much larger, and the donor nitrogen atom is only accessible on a small portion of the surface of the species. Using CPK models the pyrazinium donor nitrogen appears to extend about 3–4 Å beyond the top rim of the β-CD cavity. With the smaller cavity of the α-CD, the $ADpyz^+$ ligand would not be included as deeply as in the case of β-CD and the N-donor atom would be therefore more exposed to the solution. This would account for the larger limiting rate constant (1110 vs 910 M^{-1} s^{-1}) for the reaction of $Fe(CN)_5OH_2^{3-}$ with the $\{ADpyz\cdot\alpha\text{-}CD\}^+$ ligand.

The enthalpies of activation associated with k_1 and k_2 are the same within the experimental uncertainties, as anticipated for the rate-determining loss of the aqua ligand in both cases. The entropy of activation, however, decreases by about 17 J K^{-1} mol^{-1}, upon β-CD inclusion of the entering ligand. It has been observed previously for $Fe(CN)_5OH_2^{3-}$ [25] and $Ru(CN)_5OH_2^{3-}$ [36] substitution reactions that $\Delta S^{\ddagger}$ decreases about 8–10 J K^{-1} mol^{-1} with each unit decrease in the charge of the entering ligand. This decrease was related to an entropy change associated with the ion-pair formation prior to aqua ligand dissociation. In the present system the inclusion of the ligand reduces its apparent charge felt by the metal complex in the precursor ion-pair.

The metal-to-ligand charge transfer (MLCT) bands of substituted pentacyanoferrate(II) complexes containing aromatic N-heterocyclic ligands display solvatochromism, with a decrease in the MLCT energy (and a slight increase in ε) with a decrease in the acceptor number (AN) of the solvent.[37,38] The inclusion of the adamantyl moiety of the $Fe(CN)_5(ADpyz)^{2-}$ complex in the α- or β-CD cavity results in a bathochromic shift of the MLCT band from 656 to 672 nm. The lowering of the energy of the MLCT band is most probably due to the change in the solvation of the *N*-adamantan-1′-ylpyrazinium ligand upon entering the cavity. We have also observed bathochromic shifts in the MLCT band for pentacyanoferrate(II) complexes containing neutral N-heterocycles (such as 4-phenylpyridine and 4-benzylpyridine) in the presence of β-CD.[22] Studies in mixed aqueous–organic solvent systems indicate that there are preferential solvation effects on the spectroscopic behavior.[37,38] On going from an aqueous solution to a mixed water–acetonitrile or water–acetone solvent system, the MLCT energies decrease with an increase in the mole percent of the organic solvent (decreasing acceptor number), for both the $Fe(CN)_5(ADpyz)^{2-}$ and $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$ complexes.

The rate constant for the dissociation of coordinated $ADpyz^+$ from the $Fe(CN)_5(ADpyz)^{2-}$ complex, in the presence of 0.10 M DMSO, decreased from 2.1×10^{-4} to 7.9×10^{-5} s^{-1} for β-CD and 7.3×10^{-5} s^{-1} for α-CD. The ligand dissociation reactions of substituted pentacyanoferrate(II) complexes occur by a D mechanism, with the rate constant for loss of L^{n+} from $Fe(CN)_5L^{(3-n)-}$ being independent of the nature of the entering ligand and reaching a limiting value at high entering ligand concentrations. The relative values of the dissociation rate constants for various N-donor ligands have been discussed previously in terms of the Fe–N bond strength and the changes in ligand solvation upon dissociation.[23] The activation enthalpy for the dissociation reaction, which is related to the Fe–N bond strength, increased by 10 kJ mol^{-1} upon β-CD inclusion of $Fe(CN)_5(ADpyz)^{2-}$. While the bathochromic shift in the MLCT band for the $Fe(CN)_5(ADpyz)^{2-}$ complex upon inclusion in the β-CD cavity is also indicative of greater π-backbonding and a stronger M–L bond, there is no significant change in the energy of the d-d transition, which has previously been correlated with the rate of dissociation of L^{n+} from $Fe(CN)_5L^{(3-n)-}$ complexes.[39] A correlation between the ^{13}C chemical shift difference between the cis-CN and trans-CN resonances ($\Delta(\delta) = \delta_{cis} - \delta_{trans}$) and the MLCT energies for $Fe(CN)_5L^{(3-n)-}$ complexes, where L is an aromatic N-heterocycle, has also been reported.[40] In the present system an increase of only 0.2 ppm, from 5.9 ppm for $Fe(CN)_5(ADpyz)^{2-}$ to 6.1 ppm for the included complex, is observed. It appears, therefore, that while there may be a small increase in the Fe–N bond strength, solvent effects are likely also important. The similarities in the values of k_{-2} and the extent of the bathochromic shifts in the MLCT transition energies for the α- and β-CD included complexes suggests that the depth of inclusion is not particularly important in regards to the spectroscopic and kinetic properties of the complex.

Previous kinetic studies of the ligand dissociation reactions of substituted pentacyanoferrate(II) complexes in mixed aqueous-organic solvent systems have generally shown that the rate of neutral ligand dissociation increases as the acceptor number of the solvent is decreased.[38b,41,42] This trend has been related to the more hydrophobic nature of transition state, with the release of the aromatic N-heterocycle, compared with the ground state. In the present study the rate constants for the dissociations of $Fe(CN)_5(ADpyz)^{2-}$ and $Fe(CN)_5(Mepyz)^{2-}$ (in the absence of β-CD) show a decrease with an decrease in the acceptor number of the solvent mixture (Figure 5). With the cationic leaving ligands, the charge separation which occurs upon transition state formation would be less favored in the more nonpolar solvent mixture. There is little change observed in the dissociation rate constants for the $Fe(CN)_5\{ADpyz\cdot\beta\text{-}CD\}^{2-}$ inclusion upon addition of the organic cosolvents. As the $ADpyz^+$ leaving ligand is already solvated by the hydrophobic β-CD cavity (and forms a stronger inclusion complex with β-CD as a free ligand), the bulk solvent composition is of reduced importance. Further studies of the visible spectra and ligand dissociation rate constants of $Fe(CN)_5L^{(3-n)-}$ complexes with β-cyclodextrin and heptakis(2,6-di-*O*-methyl)-β-cyclodextrin (more soluble than β-CD) in mixed aqueous–organic solvent systems are underway in our laboratory.

With both the rate constants for the formation and ligand dissociation decreasing to a similar extent, the stability constant for the $Fe(CN)_5(ADpyz)^{2-}$ complex, with respect to ligand dissociation, remains virtually unchanged upon inclusion in β-CD, decreasing very slightly from $(1.22 \pm 0.06) \times 10^7$ M^{-1} to $(1.15 \pm 0.09) \times 10^7$ M^{-1}. The reduction potential for the $Fe(CN)_5(ADpyz)^{-/2-}$ couple, which may be related to a ratio of stability constants for the pentacyanoferrate(III) and -(II) complexes,[23] is 0.76 V (vs NHE) in both the presence and the absence of β-CD. Investigations into the effects of cyclodextrin inclusion on the kinetics of electron-exchange and electron-transfer reactions involving the $Fe(CN)_5(ADpyz)^{-/2-}$ couple and related substituted pentacyanoferrate(III/II) complex couples are in progress.

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