have intense CT bands at 15–20 kK which are almost certainly associated with charge transfer to the α-diimine units (Figure 3). Although the assignments of these bands to CT transitions associated with the various axial groups CN^-, SCN^-, etc. cannot be ruled out, this possibility seems remote. For $[Fe(CN)_6]^{4-}$, which contains only CN^- as a ligand the $t_{2g}{}^6 \rightarrow t_{2g}{}^5\ \pi^*$ transition occurs at very high energy (45.9 kK).[24] The low-spin $[Fe(NO_2)_6]^{4-}$ [25] and $[Fe(CNCH_3)_6]^{2+}$ [26] complexes have been previously reported but electronic absorption data are lacking.

For a series of bis complexes of the general formula $Fe^{II}(o\text{-phen})_2(CNBX_3)_2$, where X = CH_3, H, F, Cl, and Br, Shriver and Posner[27] demonstrated the effects of the two monodentate ligands on the α-diimine CT absorptions. The CT bands for these complexes are shifted toward higher energies relative to the dicyano compound. It was suggested that the Lewis acid adducts of CN^- are very good π-bonding ligands and that they cause a lowering of the t_{2g} energy levels relative to the cyano derivative. This accounts for an increase in the energy of the CT transition. Similar arguments were given by Hamer and Orgel[28] for $[Fe^{II}(o\text{-phen})_2(CNH)_2]^{2+}$ and $[Fe^{II}(o\text{-phen})_2(CNCH_3)_2]^{2+}$ which contain protonated and alkylated CN^- and are similar to the CNH and $CNCH_3$ derivatives of the macrocyclic complexes described here. The energies of the CT bands for both systems are in the order CNH > $CNCH_3$ > CN^-. For the entire series of [14]-tetraeneN_4 complexes the principal CT band varies with the axial ligand as follows: NO_2^- (15.0 kK), CN^- (15.6 kK), CH_3CN (17.3 kK), CH_3NC (19.5 kK), HNC (20.0 kK).

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Registry No. $[Fe([14]1,3,8\text{-triene}N_4)(CH_3CN)_2](PF_6)_2$, 55177-55-4; $[Fe([14]1,3,8\text{-triene}N_4)(Im)_2](BF_4)_2$, 55177-57-6; $Fe([14]1,3,8\text{-triene}N_4)(SCN)_2$, 55177-58-7; $[Fe([14]1,3,8\text{-triene}N_4)(Cl)_2]PF_6$, 55177-60-1; $[Fe([14]1,3,8,10\text{-tetraene}N_4)(CH_3CN)_2](PF_6)_2$, 55221-62-0; $Fe([14]1,3,8,10\text{-tetraene}N_4)(SCN)_2$, 55221-63-1; $Fe([14]1,3,8,10\text{-tetraene}N_4)(CN)_2$, 55221-64-2; $[Fe([14]1,3,8,10\text{-tetraene}N_4)(CNH)_2](SO_3CF_3)_2$, 55221-65-3; $[Fe([14]1,3,8,10\text{-tetraene}N_4)(CNCH_3)_2](PF_6)_2$, 55208-69-0; $Fe([14]1,3,8,10\text{-tetraene}N_4)(NO_2)_2$, 55177-61-2; $[Fe([14]1,3,8,10\text{-tetraene}N_4)(Cl_2)]PF_6$, 55221-67-5; $[Co([14]1,3,8,10\text{-tetraene}N_4)(Cl)_2]ClO_4$, 55177-63-4; $[Fe([14]ane N_4)(CH_3CN)_2](BF_4)_2$, 55221-69-7.

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Stereochemical Consequences of Ligand Rigidity in Nucleophilic Substitution. Reaction of Cyanide Ion with Tris(α-diimine)iron(II) Substrates[1]

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Specific stereochemical effects related to ligand rigidity appear to occur in the reactions between optically active tris(diimine)iron(II) ions and cyanide. Optical retention predominates in the reaction between cyanide and tris(2,2′-bipyridine)iron(II), which has a relatively flexible ligand, whereas earlier studies have shown a predominance of optical inversion for the correspondingly rigid 1,10-phenanthroline complex. The activation parameters (ΔH^* and ΔS^*) are higher for the retention path than for the inversion path as was also found for the 1,10-phenanthroline reaction in which inversion predominates. This trend is evident from the positive temperature dependence of the retained optical activity relative to the inverted temperature dependence of the net inversion in the 1,10-phenanthroline case.

Introduction

The reaction of optically active tris(2,2′-bipyridine)iron(II), $\Delta\text{-}Fe(bipy)_3{}^{2+}$, with aqueous cyanide has been studied in detail in order to compare the stereochemistry and relevant activation parameters with the novel inversion reaction observed previously[2] for the analogous *o*-phenanthroline complex, $\Delta\text{-}Fe(phen)_3{}^{2+}$. The bipyridine complex produces an excess of optically retained $\Delta\text{-}Fe(bipy)_2(CN)_2$ with activation parameters consistent with the *o*-phenanthroline complex studies, which under analogous conditions produce an excess of inverted $\Lambda\text{-}Fe(phen)_2(CN)_2$. The stereochemical configurations are based on the circular dichroism spectra of the π–π* transitions and assignments are based on the exciton theory.[2,3] The absolute configuration of the $Fe(phen)_3{}^{2+}$ ion[4] is in agreement with the exciton assignment.

Previous kinetics investigations of aqueous cyanide with racemic tris(diimine)iron(II) complexes[5] have shown the necessity of a composite rate law of the type

$$\frac{-d\,[Fe(\alpha\text{-diimine})_3{}^{2+}]}{dt} = (k_1 + k_2[CN^-])[Fe(\alpha\text{-diimine})_3{}^{2+}] \qquad (1)$$

but the k_1 term must include an intramolecular racemization (k_i) path plus the dissociative (k_d) path for the optically active complexes.[6]

The fact that the percent of optically active product is only linearly related to the cyanide ion concentration through a plot of (% by k_2)/(% optically active) vs. $1/[CN^-]$, where the percent by k_2 is determined from the fraction $k_2[CN^-]/(k_1 + k_2[CN^-])$, has made possible the separation of the k_2 term into retention and inversion paths. Several possible mechanisms were considered for the $[Fe(phen)_3]^{2+}$ system; however, careful consideration of the calculated activation parameters obtained for each mechanism in conjunction with chemical intuition led to an inversion–retention mechanism illustrated by eq 2–5.[2a]

$$\Delta\text{-}Fe(phen)_3{}^{2+} + CN^- \xrightarrow{k_{ret}} \Delta\text{-}Fe(phen)_2(H_2O)(CN)^+ + phen \qquad (2)$$

$$\Delta\text{-}Fe(phen)_3{}^{2+} + CN^- \xrightarrow{k_{inv}} \Lambda\text{-}Fe(phen)_2(H_2O)(CN)^+ + phen \qquad (3)$$

$$\Delta\text{-}Fe(phen)_2(H_2O)(CN)^+ \xrightarrow{k_{ar}} {}^1/_2\,\Delta\text{-}Fe(phen)_2(H_2O)(CN)^+ + {}^1/_2\,\Lambda\text{-}Fe(phen)_2(H_2O)(CN)^+ \qquad (4)$$

$$\Delta\text{-}Fe(phen)_2(H_2O)(CN)^+ + CN^- \xrightarrow{k_{di}} H_2O + \alpha\Delta\text{-}Fe(phen)_2(CN)_2 + (1-\alpha)\Lambda\text{-}Fe(phen)_2(CN)_2 \qquad (5)$$

Analogous reactions for the mirror images are also involved. This mechanism is consistent with the (% by k_2)/(% optically active) ratio being linear with $1/[CN^-]$ with

$$\text{intercept} = k_2/(k_{inv} - k_{ret}) \qquad (6)$$

and

$$\text{slope} = k_2 k_{ar}/k_{di}(k_{inv} - k_{ret}) \qquad (7)$$

where the second-order rate constant for cyanide substitution is the sum of the inversion and retention paths, i.e.

$$k_2 = k_{inv} + k_{ret} \qquad (8)$$

The logical production of both inverted and retained configurations during the reaction of Δ-$Fe(phen)_3^{2+}$ with cyanide has been discussed previously.[2a] Briefly, cyanide ion attacks the iron(II) complex resulting in a seven-coordinate intermediate (or tight ion pair) which activates ligand loss to $Fe(phen)_2(CN)_2$ via inversion and retention pathways. Inversion results from activation of the phen moiety trans to the perturbing cyanide. The concerted process involving the loss of the trans ligand with a concurrent rotation of a cis ligand makes room for the cyanide. A second cyanide substitution produces the inverted $Fe(phen)_2(CN)_2$. Retention, however, results from the loss of a phenanthroline moiety cis to the cyanide nucleophile. Addition of a second cyanide ion produces the retained product. (See Figure 2 of ref 2a for a detailed diagram.) The nonlinear $[CN^-]$ to optical activity ratio apparently results from the competitive racemization (eq 4). Only $Fe(diimine)_2(CN)_2$ has been observed as a product for either the phen[2b,5a] or the bipy[5b] tris(diimine)iron(II) reactant with aqueous cyanide under conditions comparable to those of this study. Isosbestic and isorotatory points throughout the reactions verify only one observable step.[2,5] With the $[Fe(phen)_3]^{2+}$ reaction we observed a neutral product (as determined by electrophoresis) possessing an absorption spectrum consistent with $Fe(phen)_2(CN)_2$.[2b] Subsequent to the completion of this study, Nord[7] reported that in more dilute cyanide solutions hydroxide appears to preclude the addition of the second cyanide (eq 5) prior to racemization.[7] Furthermore, even $Fe(diimine)(CN)_4^{2-}$ was detected,[7] whereas the displacement of *o*-phenanthroline or 2,2'-bipyridine by cyanide from $Fe(diimine)_2(CN)_2$ requires elevated temperatures for extended time periods.[8]

Table I. Specific Rate Constants for the Reaction of Δ-$Fe(bipy)_3{}^{2+}$ with Aqueous Cyanide as a Function of Temperature[a]

Temp, °C	$10^6 k_1$,[b] sec^{-1}	$10^6 k_1$,[c] sec^{-1}	$10^5 k_2$, $sec^{-1}\,M^{-1}$	Linear cor coeff
0.0	6.81 (0.12)	6.41 (0.15)	9.03 (0.03)	0.9994
8.0	28.0 (0.3)	27.9 (0.3)	30.5 (0.07)	0.9999
15.0	99.0 (0.9)	99.2 (0.9)	85.3 (0.4)	0.9999

[a] Ionic strength is 2.00 *M* (maintained with KCl); numbers in parentheses are standard deviations. [b] Values based on racemization experiments. [c] Values based on intercepts of weighted linear least-squares analysis of cyanide dependence.

Differences occur in the chemistry of $Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{2+}$ because of the greater flexibility of the bipyridine.[9] A unidentate diimine ligand is possible in the course of ligand substitution reactions with $Fe(bipy)_3^{2+}$ but is sterically unlikely with the $Fe(phen)_3^{2+}$ complex.[6,9] This difference was first noted in acid hydrolysis reactions of the two complexes.[6]

Experimental Section

Synthesis of Δ-Tris(2,2'-bipyridine)iron(II) Perchlorate Dihydrate. Preparation of the complex followed the procedure of Dwyer and Gyarfas[10] with the additional precautions of adding iron fillings to the ferrous sulfate solution until no iron(III) test with thiocyanate could be obtained on a test portion and conducting the reaction under a prepurified nitrogen atmosphere. Anal.[11] Calcd for $Fe(C_{10}H_8N_2)_3(ClO_4)_2\cdot 2H_2O$: C, 47.5; H, 3.69; N, 11.1. Found: C, 47.4; H, 4.07; N, 11.0.

Synthesis of Dicyanobis(2,2'-bipyridine)iron(II). This complex was prepared according to the procedure given by Schilt.[8] Anal. Calcd for $Fe(C_{10}H_8N_2)_2(CN)_2$: C, 55.7; H, 4.64; N, 17.7. Found: C, 55.8; H, 4.64; N, 17.2.

Synthesis of Potassium Tetracyanomono(2,2'-bipyridine)iron(II) Monohydrate. This complex was prepared according to the procedure given by Schilt.[8] However, the complex was dried over P_4O_{10} in vacuo for 24 hr. Anal. Calcd for $K_2[Fe(C_{10}H_8N_2)(CN)_4]\cdot H_2O$: C, 40.8; H, 2.44; N, 20.4. Found: C, 40.7; H, 2.56; N, 19.0.

Methodology. Kinetics studies, percent retention studies, computational methods, and instrumentation have been discussed previously.[2] Inasmuch as the *rac*-$Fe(bipy)_2(CN)_2$ product has limited aqueous solubility, at higher iron concentrations the solid product was filtered from the solution prior to making the rotation measurements. As in the reaction between cyanide and optically active $Fe(phen)_3^{2+}$, the precipitated product was racemic. (Although not stated explicitly in the earlier studies,[2] filtration was also used to remove some of the racemate when higher phenanthroline complex concentrations were used, too.)

Results

The reaction kinetics of $Fe(bipy)_3^{2+}$ plus cyanide have been investigated by using circular dichroism. Figure 1 illustrates the circular dichroism spectra in the region of the long-axis polarized $\pi \rightarrow \pi^*$ transition of the starting material $Fe(bipy)_3^{2+}$ and the product $Fe(bipy)_2(CN)_2$. The visible absorption spectrum of a chloroform extract of the product (16.5_0, 18.4_5, and 25.9_1 kK) agrees, within experimental error, with that of synthetically prepared $Fe(bipy)_2(CN)_2$ (16.5_8, 18.5_1, and 25.9_7 kK) and with the results of Schilt.[8]

The ultraviolet CD spectra show the characteristic positive and negative components associated with the $\pi \rightarrow \pi^*$ transitions. The existence of a nonzero isodichroic point (293 nm) throughout the reaction is indicative of an optically active product being formed in the only observable reaction step. Infinite-time product spectra have the same sign as the starting material.

The specific rate constants k_1 and k_2, which are given in Table I along with appropriate standard deviations, were determined from a linear least-squares analysis of the observed rate constants (k_{obsd}) vs. cyanide ion concentration. Plots of k_{obsd} vs. $[CN^-]$ concentration as well as the linear correlation coefficients given in Table I indicate good linear correlation over the concentration range studied. The specific rate

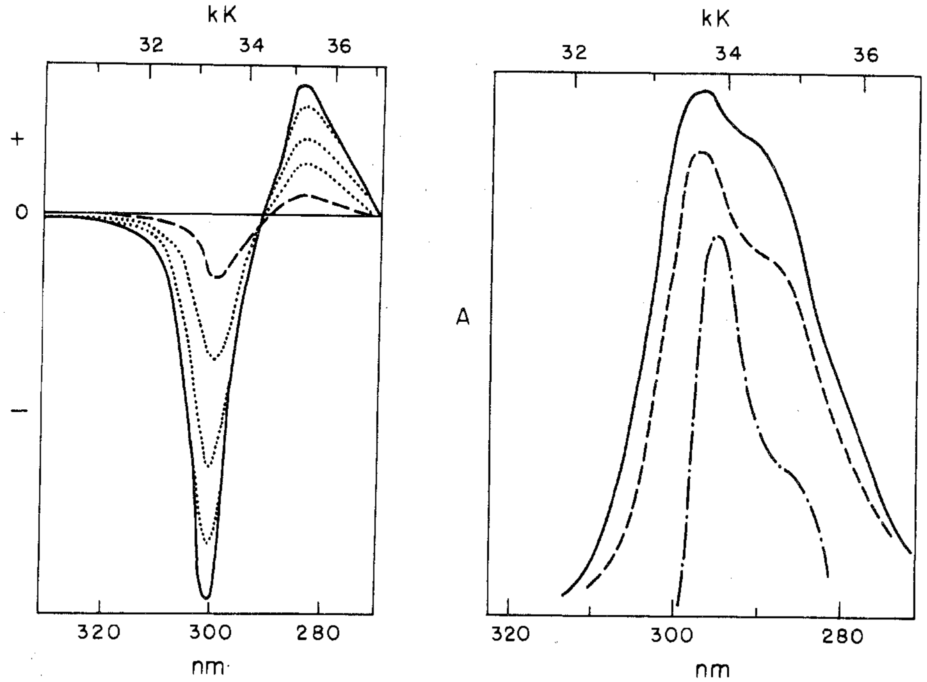

Figure 1. Circular dichroism and absorption spectra of the π-π^* region for Fe(bipy)$_3^{2+}$ (——) and Fe(bipy)$_2$(CN)$_2$ (- - -) and the analogous absorption spectrum for Fe(bipy)(CN)$_4^{2-}$ (– · – · –). Intermediate CD spectra are shown as dotted lines.

Table II. Percent Optical Retention for the Reaction of Δ-Fe(bipy)$_3^{2+}$ with Aqueous Cyanide as a Function of Temperature[a]

	% retention		
[CN$^-$], *M*	0.0°	8.0°	15.0°[b]
0.40	5.6 (0.6)	11.6 (0.5)	11.6 (0.4)
0.60	7.2 (0.8)	13.9 (0.5)	15.2 (0.9)
0.80	10.5 (0.6)	18.0 (0.9)	18.9 (1.4)
1.00	12.3 (0.8)	19.7 (0.6)	20.6 (1.7)
1.49	16.5 (0.7)	22.9 (0.7)	24.1 (1.3)
1.99	17.4 (0.5)	24.4 (1.0)	27.0 (1.4)

[a] Calculations based on two independent calculations with 320 and 345 nm as reference points using triplicate spectra, two independent experiments at each concentration and temperature, and the relationship that *R*(tris) = 2*R*(bis), where *R* is rotatory strength. [b] Three independent experiments at each concentration.

constants, as determined from observed changes in optical activity corrected for mutarotation, are within experimental error of spectroscopically measured rate constants.

Table II lists the observed net percent optical retention data with the rotatory strength of the bis complex taken as half that of the tris complex. These values were calculated from three spectra per solution. The calculation used two reference points, one where the rotation of the product is zero (320 and 345 nm) and one, at 300 nm, where the rotation is maximum, with two independent experiments for each point, except in the case of the 15° data where three experiments per point were analyzed for infinite-time rotations.

The percent retention vs. percent by the k_2 path (Figure 2) indicates a greater dependence on cyanide ion than is expected for the k_2 path, although the k_1 path yields only racemic product. As noted above, good linear correlation was observed in plots of k_{obsd} vs. cyanide concentration over the concentration range studied, thus precluding the necessity of higher order terms in cyanide concentrations. However, the percent retention can be linearly correlated with the expression

$$\% \text{ by } k_2/\% \text{ retained} = A + B/[\text{CN}^-] \qquad (9)$$

as illustrated in Figure 2. Table III lists the data and standard deviations necessary to obtain the (% by k_2)/(% retained) ratios as well as the linear least-squares analysis of these ratios vs. the reciprocal of cyanide ion concentrations.

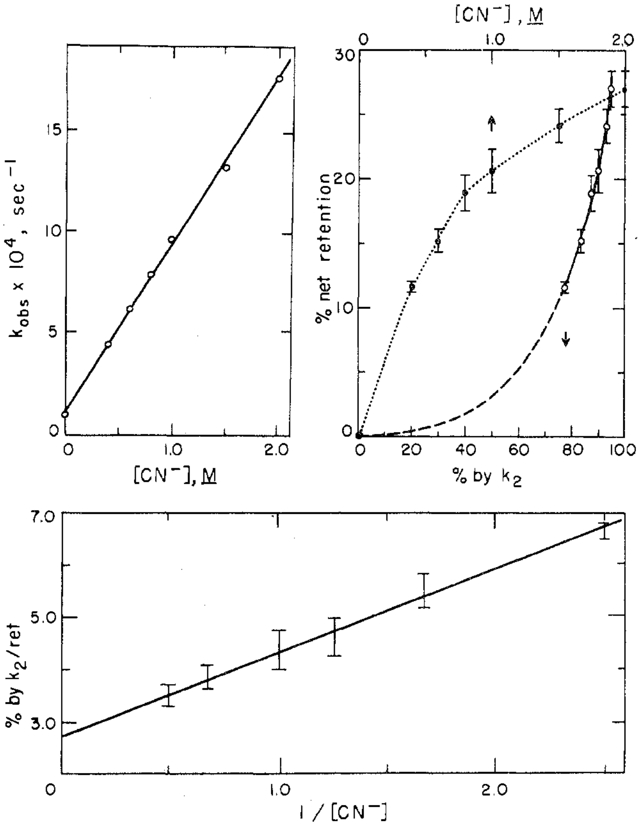

Figure 2. Plots of k_{obsd} vs. [CN$^-$] (——), % net retention at infinite time vs. [CN$^-$] (· · · · ·), % net retention vs. % of reaction by the k_2 path (- - -), and (% by the K$_2$ path)/(% net retention) vs. 1/[CN$^-$] (bottom graph) for Fe(bipy)$_3^{2+}$ plus aqueous cyanide at 15.0°.

Although racemic Fe(bipy)$_2$(CN)$_2$ precipitates at high complex concentrations, at lower complex concentrations no precipitation occurs. The results remain consistent.

Table III. Least-Squares Fit of (% by k_2)/(% retained) vs. 1/[CN⁻]

1/[CN⁻], M^{-1}	% by k_2	% ret	(% by k_2)/(% ret) Exptl	(% by k_2)/(% ret) Calcd
		0.0°		
2.50	84.9 (0.86)	5.63 (0.62)	15.1 (1.7)	14.6
1.67	89.4 (0.92)	7.24 (0.79)	12.3 (1.4)	10.7
1.25	91.8 (0.95)	10.5 (0.57)	8.75 (0.48)	8.82
1.00	93.4 (0.98)	12.3 (0.84)	7.59 (0.52)	7.66
0.671	95.4 (1.0)	16.5 (0.67)	5.78 (0.24)	6.14
0.503	96.6 (1.0)	17.4 (0.54)	5.55 (0.18)	5.36
	intercept = 3.04 (0.34); slope = 4.62 (0.47); linear cor coeff = 0.9758			
		8.0°		
2.50	81.4 (0.72)	11.6 (0.53)	7.01 (0.33)	7.26
1.67	86.8 (0.81)	13.9 (0.52)	6.23 (0.24)	5.84
1.25	89.7 (0.86)	18.0 (0.89)	4.99 (0.25)	5.13
1.00	91.6 (0.84)	19.7 (0.58)	4.65 (0.14)	4.70
0.671	94.2 (0.94)	22.9 (0.72)	4.11 (0.14)	4.14
0.503	95.6 (0.97)	24.4 (1.0)	3.91 (0.17)	3.86
	intercept = 3.00 (0.16); slope = 1.70 (0.15); linear cor coeff = 0.9854			
		15.0°		
2.50	77.5 (0.75)	11.6 (0.44)	6.68 (0.26)	6.71
1.67	83.8 (0.85)	15.2 (0.93)	5.51 (0.34)	5.39
1.25	87.3 (0.92)	18.9 (1.4)	4.62 (0.34)	4.72
1.00	89.6 (0.96)	20.6 (1.7)	4.35 (0.37)	4.33
0.671	92.8 (1.0)	24.1 (1.3)	3.85 (0.21)	3.80
0.503	94.5 (1.0)	27.0 (1.4)	3.50 (0.18)	3.53
	intercept = 2.74 (0.19); slope = 1.59 (0.15); linear cor coeff = 0.9986			

Table IV. Comparison of the k_1 and k_2 Paths with Percent Retention of $Fe(bipy)_3^{2+}$ with Cyanide at 15°

[CN⁻],[a] M	k_{obsd}	% by k_1[b]	% by k_2[c]	% retention Calcd for k_2	% retention Exptl[e]
0.00	9.90×10^{-5}	100.0	0.0	0	0
0.40	4.39×10^{-4}	22.5	77.5	11.6[d]	11.6
0.60	6.18×10^{-4}	16.2	83.8	12.5	15.2
0.80	7.87×10^{-4}	12.7	87.3	13.1	18.9
1.00	9.59×10^{-4}	10.4	89.6	13.4	20.6
1.49	1.31×10^{-3}	7.2	92.8	13.9	24.1
1.99	1.75×10^{-3}	5.5	94.5	14.1	27.0

[a] Total ionic strength is 2.00 M. [b] $k_1/k_{obsd} \times 100\%$. [c] 100% – (% by k_1). [d] Standard point, not calculated. [e] Based on the assumption that the $\pi \rightarrow \pi^*$ rotatory strength of the bis complex is 50% the rotatory strength of the tris complex.

Discussion

Reaction Stereochemistry. Through exciton theory[3] arguments, we conclude that the reaction of Δ-$Fe(bipy)_3^{2+}$ with aqueous cyanide produces a net retention of configuration in contrast to the analogous reaction of Δ-$Fe(phen)_3^{2+}$ with aqueous cyanide, which produces a net inversion of configuration.[2b] The percent retention (Table II) is calculated from the expression $([\theta]_\infty/[\theta]_0) \times 2 \times 100\%$, where $[\theta]_\infty$ is the molar ellipticity of the bis complex at infinite time, $[\theta]_0$ is the molar ellipticity of the tris complex at time 0, and the factor 2 arises from the assumption that the rotatory strength of the bis complex is 50% of that of the tris complex. The assumption is based on a prediction from simple exciton theory; however, bis complexes have rotatory strength values which range from 10 to 70% of the values for the corresponding tris species.[3,12] Although the absolute values of the percent retention may be different from the values reported, the relative values are more significant to the considerations herein.

Table V. Specific Rate Constants and Activation Parameters for the Cyanide-Dependent Retention Reaction of Δ-$Fe(bipy)_3^{2+}$

	Overall 10^5k_2	Retention–inversion 10^5k_{inv}	Retention–inversion 10^5k_{ret}
$k(0.0°)$, M^{-1} sec^{-1}	9.03 (0.03)	3.0 (0.4)	6.0 (0.4)
$k(8.0°)$, M^{-1} sec^{-1}	30.5 (0.07)	10.2 (0.6)	20.3 (0.6)
$k(15.0°)$, M^{-1} sec^{-1}	85.3 (0.40)	27.0 (2.0)	58.2 (2.0)
E_a, kJ mol^{-1}	97.9 (0.4)	95.4 (0.8)	99.2 (1.3)
ln A (A in M^{-1} sec^{-1})	33.8 (0.25)	31.7 (0.4)	33.9 (0.5)
Linear cor coeff	–1.000	–1.000	–0.9999
$\Delta H^\ddagger$, kJ mol^{-1}	95.4 (0.4)	92.9 (0.8)	96.7 (1.2)
$\Delta S^\ddagger$, J mol^{-1} deg^{-1}	28 (2)	10 (3)	29 (4)

Analogous to the $Fe(phen)_3^{2+}$ reaction, the k_2[CN⁻] term does not directly correlate with the observed retention for the $Fe(bipy)_3^{2+}$ reaction (Table IV). If the retention were a direct function of the k_2[CN⁻] term, an increase of only 2.5% (from 11.6 to 14.1%) should have been observed over the concentration range 0.40 to 1.99 M CN⁻ because the percent of the reaction by this path is already over 77% at 0.40 M CN⁻. However, the experimental percent retention more than doubles over this concentration range indicating a much greater dependence on [CN⁻] as is the case for the inversion reaction of $Fe(phen)_3^{2+}$ with cyanide.[2] However, an excellent linear correlation is obtained at each temperature for the plots of (% by k_2)/(% retained) vs. 1/[CN⁻], Table III.

An inversion–retention mechanism and an inversion–racemization mechanism were previously proposed[2] to explain the inversion reaction of $Fe(phen)_3^{2+}$ with cyanide. Both mechanisms were found to be consistent with the analogous relationship (% by k_2)/(% inversion) vs. 1/[CN⁻]. As noted recently,[2a] the molecular stereochemical considerations plus the present bipyridine results favor the inversion–retention mechanism, although more complex retention, inversion, and racemization activations cannot be excluded.

Activation Parameters for the k_2 Path. Table V lists the specific rate constants for the inversion–retention mechanism as well as the total k_2 path and activation parameters. Burgess,[6] in a recent spectroscopic study of the reaction of *rac*-$Fe(bipy)_3^{2+}$ with CN⁻ over the temperature range 25.3–46.0° in solutions maintained at constant ionic strength of 0.10 M, reported the following activation parameters: $\Delta H^\ddagger = 96.1 \pm 3.3$ kJ mol^{-1} and $\Delta S^\ddagger = 38$ J mol^{-1} deg^{-1}. Treatment of the Burgess data with the weighted least-squares computational methods of the present study gives the following values: $\Delta H^\ddagger = 96.1 \pm 1.7$ kJ mol^{-1} and $\Delta S^\ddagger = 36 \pm 2$ J mol^{-1} deg^{-1}. Results of this investigation (Table V) for the same reaction with the use of optically active material in solutions maintained at 2.0 M ionic strength over the temperature range 0.0–15.0° gives very good agreement. The change in ionic strength may account for the small $\Delta S^\ddagger$ change.

Inversion–Retention Mechanism. The inversion–retention mechanism discussed earlier in this paper offers the most logical explanation of the observed inversion occurring during cyanide substitution of $Fe(phen)_3^{2+}$. The extension of this mechanism to the bipy system is illustrated by eq 10–13, where α is the

$$\Delta\text{-Fe(bipy)}_3^{2+} + \text{CN}^- \xrightarrow{k_{\text{ret}}} \Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{bipy} \qquad (10)$$

$$\Delta\text{-Fe(bipy)}_3^{2+} + \text{CN}^- \xrightarrow{k_{\text{inv}}} \Lambda\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{bipy} \qquad (11)$$

$$\Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ \xrightarrow{k_{\text{ar}}} {}^1/_2\Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + {}^1/_2\Lambda\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ \qquad (12)$$

$$\Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{CN}^- \xrightarrow{k_{\text{di}}} \text{H}_2\text{O} + \alpha\Delta\text{-Fe(bipy)}_2(\text{CN})_2 + (1-\alpha)\Lambda\text{-Fe(bipy)}_2(\text{CN})_2 \qquad (13)$$

fraction of retention in the anation reaction. Analogous expressions exist for the Λ isomers. The k_{ar} path may include racemizations of Δ-$Fe(bipy)_2(OH)CN$ as well and any traces of anionic products.

The steady-state treatment of this mechanism applying the assumptions used previously[2] [i.e., (1) α equals unity, (2) the rotatory strength of the bis complex is half the rotatory strength

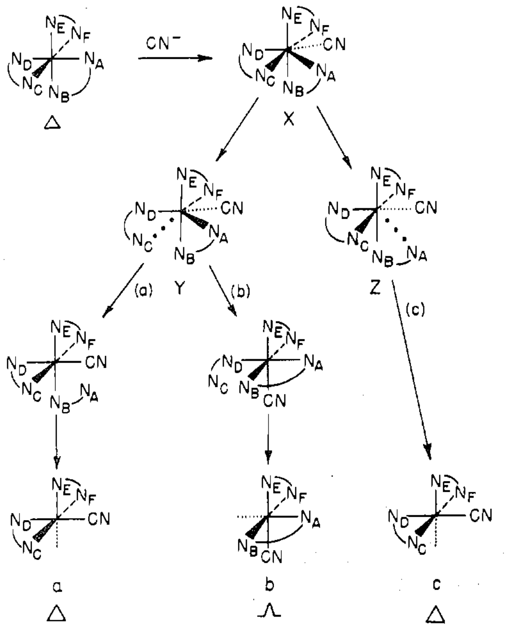

Figure 3. Proposed retention paths (a) and (c) and inversion path (b) for the nucleophilic cyanide attack on Δ-tris(bipyridine)iron(II). Intermediates a, b, and c are assumed to add water and/or cyanide without further stereochange except for the racemization included in k_{ar}.

of the tris complex, and (3) the signs of the circular dichroic spectrum can be treated according to exciton theory] permits the calculation of k_{ret} and k_{inv} from their relation to A and B of expression 9 as was done for the phenanthroline complex previously (Appendix I of ref 2a), except that the difference terms are now $k_{ret} - k_{inv}$

$$\text{intercept} = k_2/(k_{ret} - k_{inv}) \quad (14)$$

$$\text{slope} = k_2k_{ar}/k_{di}(k_{ret} - k_{inv}) \quad (15)$$

The activation parameters calculated for the inversion–retention mechanism for $Fe(bipy)_3^{2+}$ (Table V) are consistent with the inversion–retention results[2] for $Fe(phen)_3^{2+}$. The inversion process[2] involves the concerted displacement of a ligand trans to the perturbing cyanide ion plus a rotation of one of the cis ligands. Because both nitrogens of the trans ligand are "loosened", the activation energy should be lower for the inversion process than for the retention process, which involves only the displacement of a cis ligand with only one nitrogen perturbed. If this simple picture is operative in both systems, the predominance of retention over inversion for $Fe(bipy)_3^{2+}$ apparently results from increased flexibility of bipy over phen, which allows the formation of a unidentate bipy.[6,9] Unidentate coordination will alter the picture of the inversion–retention processes, which were originally presented for the inversion reaction.[2a] These variations for the $Fe(bpy)_3^{2+}$ reaction are shown in Figure 3. The CN⁻ perturbed intermediate X, which is common for both systems, can now form two additional intermediates, Y and Z, where bipy is unidentate. Such unidentate intermediates are impossible for the $Fe(phen)_3^{2+}$ ion, in which both donors must leave simultaneously.

With respect to path (c) of Figure 3, perturbation of the complex by the incoming cyanide (intermediate X) can loosen N_a (or the symmetry equivalent N_f), which produces intermediate Z. Because N_a cannot compete with the strongly nucleophilic cyano ligand, the N_a–N_b ligand of $Fe(bipy)_3^{2+}$ will be left dangling until the other end dissociates. Addition of a second cyanide ion produces a retained product. This increased flexibility allows more retention than in the $Fe(phen)_3^{2+}$ reaction, because only N_a, N_c, and N_f should be loosened by the cyanide perturbation.[2b] Thus, the loss of a cis ligand, which produces retention, should occur with an enhanced probability.

The unidentate inversion path (b) of Figure 3 requires extensive movement of N_b and cyanide (which correlates with the lower frequency factor or entropy of activation for the inversion path). Loss of N_c–N_d followed by or concurrent with the rapid addition of the second CN⁻ completes the inversion. N_e is symmetrically equivalent to N_b and could undergo an analogous inversion reaction. The other inversion path that is possible for the $Fe(phen)_3^{2+}$ reaction (path a of Figure 2 of ref 2a) is less likely if N_c–N_d is a dangling unidentate ligand when N_a attempts to move, as in intermediate Y. That is, in the $Fe(phen)_3^{2+}$ reaction, when N_a moves, it ends up in position d (because c is sterically hindered). In the present reaction, attachment of N_a at position c should also be sterically hindered and d is occupied, so movement of N_a to make room for the cyano ligand will probably produce a dangling N_a and a reattached N_c, as shown in path (a) of Figure 3. This intermediate is identical with intermediate Z of path (c) and leads to retention as noted above. Naturally, loss of N_c–N_d before N_a moves would give inversion as in the $Fe(phen)_3^{2+}$ reaction.

The net effect of the unidentate bipyridine ligands is an increase in retention and a decrease in inversion. Experimentally, the retention predominates for the flexible bipyridine complex.

Perturbation by the incoming CN⁻ causes only one nitrogen, N_a (or the symmetrically equivalent N_f), of the cis ligands to become loosened.[2] Thus, the loss of a cis ligand in one step should be more difficult than the loss of the trans ligand, for which both donors are loosened by the electronic charge. The seemingly higher activation energy for the retention paths of both the $Fe(phen)_3^{2+}$ and the $Fe(bipy)_3^{2+}$ reactions is in agreement with this reasoning. However, the lower activation energy for retention during the $Fe(bipy)_3^{2+}$ reaction compared to the $Fe(phen)_3^{2+}$ reaction apparently results from the unidentate behavior of bipyridine.

Retention–Racemization Mechanism. The linear relationship (% by k_2)/(% retained) vs. 1/[CN⁻] can be fit to another mechanism, retention plus racemization illustrated by eq 16–19.

$$\Delta\text{-Fe(bipy)}_3^{2+} + \text{CN}^- \xrightarrow{k_{2ret}} \Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{bipy} \quad (16)$$

$$\Delta\text{-Fe(bipy)}_3^{2+} + \text{CN}^- \xrightarrow{k_{2rac}} rac\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{bipy} \quad (17)$$

$$\Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{CN}^- \xrightarrow{k_{di}} \Delta\text{-Fe(bipy)}_2(\text{CN})_2 + \text{H}_2\text{O} \quad (18)$$

$$\Delta\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ \xrightarrow{k_{ar}} rac\text{-Fe(bipy)}_2(\text{H}_2\text{O})(\text{CN})^+ \quad (19)$$

The same assumptions used in the retention–inversion mechanism apply here, namely, 100% retained anation, 50% rotatory strength for the product, and configurations by exciton theory. The specific rate constants given in eq 16–19 can be related to A and B of eq 9, as was done in Appendix 2 of ref 2a, for the inversion–racemization mechanism by replacing the inversion step with a retention step. The results are given by eq 20 and 21, where k_2 is the observed cyanide-dependent

$$A = k_{2rac}/k_{2ret} \quad (20)$$

$$B = k_2k_{ar}/k_{2ret}k_{di} \quad (21)$$

specific rate constant and is equal to $k_{2ret} + k_{2rac}$.

Comparison of activation parameters for the inversion–racemization mechanism[2] with the retention–racemization mechanism (Table V) shows a lack of consistency, particularly with the $\Delta S^{\ddagger}$ values. Logically, racemization occurs by a more disordered process than either retention or inversion;[2] hence, $\Delta S^\ddagger$ for the racemization path should be more positive than for the retention or inversion path. For the inversion reaction of $Fe(phen)_3^{2+}$ with cyanide[2] $\Delta S^\ddagger(k_{2i}) = -16.0$ J mol^{-1} deg^{-1} and $\Delta S^\ddagger(k_{2r}) = 46.8$ J mol^{-1} deg^{-1}, consistent with the disorder expectations. However, for the retention of $Fe(bipy)_3^{2+}$ $\Delta S^\ddagger(k_{2ret}) = 35.1$ J mol^{-1} deg^{-1} and $\Delta S^\ddagger(k_{2rac}) = 15.9$ J mol^{-1} deg^{-1}, which is inconsistent with the above reasoning. Although the inversion–racemization and retention–racemization mechanisms are mathematically sound, the necessity of requiring the two opposites for two analogous species causes us to reject these mechanisms as being logical choices.

Validity of Configurational Assignments. The possibility exists that the exciton components of the long-axis polarized $\pi \rightarrow \pi^*$ ligand transitions may become reversed because of anomalous spectral shifts.[12,13] Figure 1 illustrates the absorption spectra of $Fe(bipy)_3^{2+}$, $Fe(bipy)_2(CN)_2$, and $Fe(bipy)(CN)_4^{2-}$. Comparison of the three spectra reveals a slight, if at all significant, energy shift between the tris and bis complexes, although a more pronounced shift is observed between the bis and mono complexes. However, because a regular trend is observed in the absorption spectra for this series of iron(II) complexes, a reversal of components is not expected. Furthermore, the exciton splitting is appreciably greater than the total shift of this series;[3a,d] hence, any anomalous spectral shift should become readily evident.

Hawkins and coworkers[12,13] have also suggested that vibronic coupling may reduce the exciton splitting and possibly alter the assignments, but Mason[3c] has recently noted that the CD spectrum of $Fe(bipy)_3^{2+}$ does not show any vibrational structure at 80°K. Recent molecular orbital calculations[14,15] as well as intermediate exciton coupling calculations,[4c,d] which allow for vibronic coupling, are both in agreement with the simple exciton theory for the iron(II) α-diimines. Furthermore, the correlation of the circular dichroism and magnetic circular dichroism spectra[16] of iron(II) α-diimines is also in agreement with the theory. Thus, sufficient evidence is available which supports the exciton theory predictions and justifies the current assignments for the tris and bis complexes.

Conclusion

The inversion–retention mechanism is completely consistent with the experimental observations and theoretical calculations. The activation parameters are in agreement with the inversion–retention parameters for $Fe(phen)_3^{2+}$ as is logical for the two similar ligands. The temperature dependence supports this conclusion. Although the reaction of $Fe(phen)_3^{2+}$ with cyanide produces a net inversion of configuration while the same reaction with $Fe(bipy)_3^{2+}$ produces a net retention,[17] the difference is ascribed to the greater flexibility of the bipy ligand which permits unidentate coordination. Sufficient alteration of the reaction paths because of unidentate coordination results in changes in the relative rates of retention and inversion.

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Registry No. Δ-$Fe(bipy)_3^{2+}$, 55122-50-4; Δ-$Fe(bipy)_2(CN)_2$, 55101-89-8; $Fe(bipy)(CN)_4^{2-}$, 17455-56-0; CN^-, 57-12-5.

References and Notes

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(17) The inability of Nord[7] to observe either the inversions or the retentions at low concentrations (0.14 M CN^- or less) is not surprising. Our early attempts to observe optical activity in the visible region led to the observation that the isorotatory points and the resulting infinite-time spectra were not far removed from the base line even at much higher concentrations.[2b] The observed inversion rotation at 0.1 M CN^- for $Fe(phen)_2(CN)_2$ in the π–π^* region, where higher rotatory strengths occur, is only 0.6% of the rotation of the $Fe(phen)_3^{2+}$ ion or 1.2% inversion from the 1:2 rotatory strength relationship.[2] The dashed line in Figure 2 of this paper is a calculated interpolation of activity vs. % by k_2 based on the (% by k_2)/(% retained) vs. 1/[CN^-] parameters. At 0.1 M CN^- the rotations would be quite low. Furthermore, the rotatory strengths in the visible region are less than in the π–π^* region, and the Perkin-Elmer Model 141 does not match the Cary 60 (modified) for sensitivity. Finally, the hydroxide problem noted by Nord[7] occurs outside the range of hydroxide ion concentrations important in our studies.[2a]