which is to be compared to 0.05 M^{-1} sec^{-1} for the reaction of pyrazine with $[Ru(NH_3)_5H_2O]^{2+}$. The difference between SO_3^{2-}, which labilizes trans and delabilizes cis, and OH^-, which exerts approximately equal labilizing effects at the two positions, is noteworthy. If it is assumed that reaction proceeds through a pentacoordinated intermediate, say a tetragonal pyramid, the difference can be ascribed to a marked preference on the part of SO_3^{2-}, but not of OH^-, for a site at the apex rather than the base of the intermediate. This suggestion is obviously not an explanation and is offered only as suggesting a direction to pursue in looking for an explanation.

Attention has already been drawn to the magnitude of the labilizing effect on two saturated ligands when NH_3 in trans position is replaced by SO_3^{2-}. When the groups being replaced are π acids, an effect in addition to that operating with saturated ligands may come into play. This effect as it is manifested in affinities has already been recognized in other systems—note that though K_{eq} for the reaction of N_2 with $Ru(NH_3)_5H_2O^{2+}$ is *ca.* 10^4, replacement of a single NH_3 by pyridine so greatly reduces the affinity of N_2 for Ru(II) that no evidence of complex formation is observable with N_2 at 1 atm (this amounts to a reduction in K_{eq} by a factor of at least 10^2). Similar large effects on affinities are noted in the present system. The value of K_{eq} for the reaction of isn with $[Ru(NH_3)_5H_2O]^{2+}$ is $>10^8$, and for pz it is expected to be of the same order of magnitude.[10] The present work shows that with SO_3 trans to these ligands, the values of K_{eq} are 4×10^3 and 3×10^3, respectively. The effect of SO_3^{2-} can be attributed at least in part to its role as a π acid. To the extent that a ligand absorbs electron density from a πd orbital, back-bonding to another ligand using the same orbital will be weakened. It is not possible with present knowledge to factor the overall effect of SO_3^{2-} on the bonding, say of isn, into the component pertaining to saturated ligands and that arising from back-donation. Such factoring may not be possible in principle; the so-called synergistic effect is likely to be strong for SO_3^{2-}, with σ-bonding formation strongly promoting back-donation. Some insight into the matter would be provided by studies of the cis cases. The effects arising from back-donation would be only slightly affected but others would be strongly altered. Such studies have not yet been done and might prove to be difficult because they would undoubtedly be complicated by loss of NH_3 in the position trans to SO_3^{2-}.

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Registry No. *trans*-$[Ru(NH_3)_4SO_2Cl]Cl$, 23346-07-8; *trans*-$[Ru(NH_3)_4(SO_2)isn](CF_3SO_3)_2$, 51175-00-9; *trans*-$[Ru(NH_3)_4(SO_2)pz](C_7H_7SO_3)_2$, 51271-76-2; *cis*-$[Ru(NH_3)_4(SO_2)H_2O](PF_6)_2$, 51175-02-1; *trans*-$[Ru(NH_3)_4(SO_2)H_2O]^{2+}$, 51175-03-2; *trans*-$[Ru(NH_3)_4(HSO_3)H_2O]^+$, 51202-30-3; *trans*-$[Ru(NH_3)_4(SO_3)H_2O]$, 51175-04-3; $Ru(NH_3)_5SO_3$, 51174-85-7; *cis*-$[Ru(NH_3)_4(SO_3)H_2O]$, 51174-86-8; $[Ru(NH_3)_5SO_2]Cl_2$, 13874-06-1; *trans*-$[Ru(NH_3)_4(SO_3)isn]$, 51174-87-9; *trans*-$[Ru(NH_3)_4(SO_3)pz]$, 51174-88-0; *trans*-$[Ru(NH_3)_4(SO_3)(pzMe)]^+$, 51174-89-1; $[Ru(NH_3)_3pzSO_3H_2O]$, 51174-90-4.

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Activation Parameter Separation through Stereochemical Observation. Inversion Reaction of Tris(*o*-phenanthroline)iron(II) with Cyanide[1]

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Observation of the product stereochemistry of the reaction between $Fe(phen)_3^{2+}$ and CN^- as a function of temperature and comparison with the rate of mutarotation under the same conditions has allowed the separation of the second-order term into retention (k_{ret}) and inversion (k_{inv}) paths possessing the following activation parameters: k_{inv}, $E_a = 23.2 \pm 0.8$ kcal/mol, $\ln A = 33.6 \pm 1.4$ (A in M^{-1} sec^{-1}), $\Delta H^\ddagger = 22.6 \pm 0.8$ kcal/mol, $\Delta S^\ddagger = 6.2 \pm 2.7$ eu; and for k_{ret} the respective values are 24.5 ± 0.3, 35.4 ± 0.5, 23.9 ± 0.3, and 9.8 ± 1.0. Logical mechanistic considerations, activation parameters, hydroxide ion independence, and linear correlations (>0.999) cause us to favor this mechanism over several other possibilities. The entropies of activation lend support to the optical inversions being true chemical inversions and to the validity of exciton theory for these species.

Introduction

Cyanide ion reacts with optically active tris(*o*-phenanthroline)iron(II) to give an optically inverted dicyanobis(*o*-phenanthroline)iron(II) product.[2] This Bailar inversion[3] reaction is of prime importance for several reasons including the following: (1) the reaction exhibits a temperature-dependent stereochemistry and should allow an intimate look at the activated complex *via* appropriate activation parameters; (2) the reaction extends the octahedral, Bailar inversion reactions to d^6 systems other than cobalt(III);[3] (3) the product, which is several orders of magnitude more stable than the reactant, has a racemization half-life of 2 months in water at room temperature[2] so that accurate isomer data[4] are possible; and (4) nucleophilic dependence for octahedral substitution reactions in water is uncommon for complexes

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(1) Preliminary data presented at the Kinetics and Mechanisms of Substitution Reactions of Metal Complexes Symposium at the Northeast Regional Meeting of the American Chemical Society, Buffalo, N. Y., Oct 1971. Abbreviations used: phen, *o*-phenanthroline; bipy, 2,2′-bipyridine; PBA, α-(2-pyridyl)benzylideneaniline.

(2) R. D. Archer, L. J. Sudyam, and D. D. Dollberg, *J. Amer. Chem. Soc.*, **93**, 6837 (1971).

(3) (a) J. C. Bailar, Jr., and R. W. Auten, *J. Amer. Chem. Soc.*, **56**, 774 (1934); (b) J. C. Bailar, Jr., *Rev. Pure Appl. Chem.*, **16**, 91 (1966); (c) R. D. Archer, "Coordination Chemistry," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 18.

(4) Modification of the Cary 60 for MCD studies included the installation of an end-on photomultiplier detection system, which has improved the signal to noise ratio for low rotations by a factor of about 4.

in which conjugate base hydrolysis is impossible.[5]

The reaction between $\mathrm{Fe(phen)_3}^{2+}$ and cyanide is not a simple substitution reaction. The logical aquocyanobis(*o*-phenanthroline)iron(II) intermediate is not observed, apparently because the intermediate aquocyano complex reacts rapidly with a second cyanide ion.[2,6] The reaction has both cyanide-independent and cyanide-dependent components with specific rate constants k_0 and k_1, respectively[2,6]

$$-\mathrm{d}[\mathrm{Fe(phen)_3}^{2+}]/\mathrm{d}t = \{k_0 + k_1[\mathrm{CN}^-]\}[\mathrm{Fe(phen)_3}^{2+}] \qquad (1)$$

Furthermore, *the observed per cent of inverted product is not directly related to the per cent which reacts by the cyanide-dependent path*,[2] even though the inverted product must come from the cyanide-dependent path—the k_0 term gives only racemic products. The lack of a simple proportionality is evident by comparing the data for 0.4 and 2.0 *M* cyanide ion solutions. Even in the 0.4 *M* solutions almost 90% of the tris complex is already reacting through the cyanide-dependent path (see Table II of ref 2), but the observed inversion is fairly small. The per cent of inverted product more than doubles for the reactions in 2.0 *M* cyanide ion, even though the reaction *via* the cyanide-dependent path has increased by only a few per cent over that at 0.4 *M* cyanide ion. *However, a plot of the ratio of the per cent of reaction by the k_1 path to the observed inversion percentage vs. the reciprocal of the cyanide ion concentration yields a straight line*,[2] which is consistent with several mechanistic possibilities.

The study of the temperature dependence of the reaction stereochemistry and the rate of stereochemical change was undertaken in order to understand more fully the inversion reaction. The results have allowed us to pick an inversion-retention mechanism, in which loss of the phen moiety trans to the nucleophilic cyanide produces an inverted product as detailed before,[2] whereas loss of one of the cis phen ligands produces a retained product, after subsequent addition of a second cyanide ion. The latter step occurs in competition with racemization of the aquocyano species. Several other mechanistic possibilities have been ruled out by experiment, by activation parameters, or by logic.

Experimental Section

1. Synthesis of Λ-Tris(*o*-phenanthroline)iron(II)[7] Perchlorate Trihydrate. The complex was prepared according to the procedure of Dwyer and Gyarfas[8] with the following modification. The addition of the *o*-phenanthroline to solutions of ferrous sulfate heptahydrate was performed in the presence of iron powder under a nitrogen atmosphere to prevent contamination by traces of iron(III) complexes. Similar precautions were taken in the preceding study with the other optical isomer.[2]

Anal. Calcd for $\mathrm{Fe(C_{12}H_8N_2)_3(ClO_4)_2 \cdot 3H_2O}$: C, 50.90; H, 3.56; N, 9.89. Found:[9] C, 51.16; H, 3.61; N, 9.90.

2. Kinetic Studies. Solution preparation was identical with that previously reported.[2] The solutions were transferred with syringes to a jacketed 1-cm quartz cell maintained at constant temperature to within 0.2°. Circular dichroism spectra in the region 260–330 nm were recorded as a function of time (with t_0 the time of mixing in the cell). When the reaction was essentially complete (based on small values of θ), the solution was allowed to warm to room temperature for approximately 1 hr to allow for racemization of any remaining tris species. (Actually mutarotation occurs, but appreciably less optical activity is obtained at room temperature.) A final spectrum was then run to obtain infinity values for θ. The same preparative, transfer, and spectral procedures were used to follow the racemization of the tris complex in 2.00 *M* KCl at each temperature.

3. Per Cent Inversion Studies. Data for per cent inversion calculations were obtained as above except that a second aliquot was added to a 2.00 *M* KCl solution each time and the circular dichroism of that portion measured as a function of time in order to obtain reliable θ_0 values while the first aliquot was maintained in a thermostated bath for at least 10 half-lives prior to obtaining the infinity values. The rotational strength of the bis complex was assumed to be 50% that of the tris complex as before.[2]

A possible effect of hydroxide ion on the inversion was checked by preparing a series of solutions with constant hydroxide concentration (6×10^{-3} *M* as determined from pH measurements) and varied cyanide concentrations through the addition of KOH and/or water to KCN solutions prepared as above. The series ranged from 0.30 ml of 0.10 *M* KOH added to the 0.40 *M* KCN solution to 0.30 ml of water added to the 2.00 *M* KCN solution. The cyanide concentrations were corrected for dilution and hydrolysis and "infinite time" solutions were measured, as before, after 2 days of reaction in an ice bath followed by warming to room temperature.

A second set of solutions was prepared with approximately constant cyanide concentrations and varying hydroxide concentrations by diluting 10.00-ml portions of 2.00 *M* KCN solution to 10.50 ml with various combinations of water and 0.10 *M* KOH. The hydroxide concentrations were calculated from the hydrolysis equilibrium and inversions at infinite time were measured as before. The solutions were incubated near 0°, but temperature control was uncertain.

4. Computational Methods. A program CIRKIN, which was written in UMASS Fortran,[10] was used to analyze the rate data and to obtain specific rate constants utilizing a weighted, linear, least-squares analysis subroutine LINFIT,[11] where the weighting factor is $1/\sigma^2$. The main program converts the experimental data, *i.e.*, base line corrections, θ_∞ values, and θ_t values at 272 and 285 nm, into the form $-\ln(\theta_t - \theta_\infty)$ and then performs a linear least-squares analysis on this quantity *vs.* time using LINFIT. The results of the LINFIT analysis are the slope, the intercept, their calculated standard deviations, and an appropriate linear correlation coefficient for a check on the validity of the data and/or analysis.

For racemization studies of Λ-$\mathrm{[Fe(phen)_3](ClO_4)_2}$ the data were transformed by the program to k_0 = slope and θ_0 = exp(intercept). For the cyanide-containing solutions the same calculation provided k_{obsd} = slope. The observed rate $k_{\mathrm{obsd}} = k_0 + k_1[\mathrm{CN}^-]$; *cf.* ref 2. Analysis of k_{obsd} *vs.* $[\mathrm{CN}^-]$ yielded k_1(obsd) = slope and provided a check on k_0 = intercept.

Activation parameters were obtained by standard procedures.[12] In order to obtain realistic values of standard deviations for each activation parameter, plots of $\ln(k + \sigma)$ *vs.* time were made, where σ is the standard deviation of k. Slopes and intercepts from weighted least-squares calculations gave the activation energies and $\ln A$ values. Hydrolysis corrections, where necessary, were calculated from literature data,[13] which checked with pH measurements in our laboratory.

5. Instrumentation. Circular dichroism spectra were obtained on a Cary 60 spectropolarimeter fitted with a circular dichroism accessory and a modified cell holder which accepts standard, jacketed, one-piece quartz absorption cells. The instrument has an end-on photomultiplier detection system for maximum signal to noise ratios, which is important for low rotations. All circular dichroism spectral base lines were recorded using 2.00 *M* KCl and all measurements used are for dynode voltages at less than 0.40 kV (absorbance <2). A refrigerated Forma constant-temperature bath was used to maintain constant temperature in the jacketed cells.

Results

The experimental k_0 and k_1 values derived by a least-squares

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(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 3.

(6) D. W. Margerum and L. P. Morganthaler, *J. Amer. Chem. Soc.*, 84, 705 (1962).

(7) The absolute configuration of the cation was determined by A. Zalkin, D. H. Templeton, and T. Ueki, *Inorg. Chem.*, 12, 1641 (1973). The nomenclature follows the recommendations of the IUPAC committe; see, *Inorg. Chem.*, 9, 1 (1970).

(8) F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. N. S. W.*, 83, 263 (1949).

(9) Chemical analyses by the late Mr. Charles Meade, University of Massachusetts Microanalytical Laboratory.

(10) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences," McGraw-Hill, New York, N. Y., 1969, p 104.

(11) UMASS Fortran is a Fortran IV simplification used in the time-sharing system at the University of Massachusetts in conjunction with CDC 3800 computers. CIRKIN is on file and is available by contacting the authors.

(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 5.

(13) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, No. 17, 107 (1964); *cf.* R. W. Harman and F. P. Worley, *Trans. Faraday Soc.*, 20, 502 (1925).

evaluation of the observed rate constants *vs.* the cyanide ion concentrations are given in Table I along with appropriate standard deviations. The linearity from 0.00 through 2.00 *M* is evident from plots of the specific rate constants *vs.* the cyanide ion concentrations with no significant deviation at either end at any temperature. As noted previously,[2] these rates, which have been obtained from the changes in optical activity corrected for mutarotation, are within experimental error of spectroscopically measured rates.

Table II lists the observed *net* optical inversions, expressed as percentages, with the rotatory strength of the product bis complex approximated as half the rotatory strength of the tris complex and called simply per cent inverted. The corresponding standard deviations are also given. Additional values of 1.2, 2.6, and 3.8% were obtained for 0.1, 0.2, and 0.3 *M* solutions at 15.0° but have not been listed in Table II. The per cent inversions are a little lower than reported previously[2] for 0.5° because of several factors, namely, the improved stability of the circular dichroism instrument through an end-on photomultiplier system (the noise appeared to enhance small signals), a smaller base line correction for 310 nm, and the use of a weighted least-squares analysis technique. Significant decreases in the net inversion are observed with increasing temperature for all concentrations above 0.4 *M* in cyanide.

Figure 1 shows the curvature in a per cent inverted *vs.* [CN$^-$] plot of the 15.0° data and the fine fit for (% by k_1)/(% inversion) for the same data. (Table III of ref 2 has analogous data for 0.5°.) Therefore, Table III lists the data and standard deviations necessary to obtain the (% by k_1)/(% inverted) ratios and the fit *vs.* the reciprocals of cyanide ion concentrations. Table IV shows that hydroxide ion concentrations do not appreciably affect the stereochemistry in the oxygen-free solutions used in this study.

Another set of experiments in which the cyanide ion concentration was held constant at 1.90 *M* and the hydroxide ion concentration was varied from 6×10^{-3} to 1.1×10^{-2} *M* resulted in inversions from 12.2 (0.5) to 11.9 (0.4)%, a minor change, if any, for almost doubling the hydroxide ion concentration.

Corrections for hydrolysis were made by plotting literature[13] data *vs.* temperature and were checked with pH measurements in our laboratory. Values of 1.7×10^{-5}, 1.9×10^{-5}, and 2.1×10^{-5} were determined for 0 to 0.5, 8.0, and 15.0°, respectively.

No evidence for $\text{Fe(phen)(CN)}_4{}^{2-}$ has been observed in this study, nor were any complications by this complex noted in previous studies.[2,6]

Discussion

In order to evaluate the reaction between optically active $\text{Fe(phen)}_3{}^{2+}$ and cyanide, a number of mechanistic possibilities were considered. As noted previously[2] a simple second-order term does not fit the inversion data. Plots of (% by k_1)/(% inverted) *vs.* the reciprocals of the cyanide concentrations give good straight lines at all three temperatures. This relationship allows us to deduce what happens to the associative cyano-activated complex subsequently. We were limited to a maximum of 15° by the racemization rate of the reactant. The rate requires extensive extrapolation to determine the zero-time rotation at higher temperatures and causes larger errors.

1. **Inversion-Retention Mechanism.** A mechanism which fits the linearity between (% by k_1)/(% inversion) and 1/[CN$^-$] is illustrated by eq 2-5 where the reactions for the Λ isomer are given, with the corresponding reactions for the Δ isomers indicated in parentheses when different, and where α is the fraction of retention in the anation reaction.

$$\Lambda(\Delta)\text{-Fe(phen)}_3{}^{2+} + \text{CN}^- \xrightarrow{k_{\text{ret}}} \Lambda(\Delta)\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{phen} \tag{2}$$

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

$$\Lambda(\Delta)\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ \xrightarrow{k_{\text{ar}}} {}^1/_2\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ + {}^1/_2\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ \tag{4}$$

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

A steady-state treatment of this mechanism using the assumptions used previously[2] (*i.e.*, that $\alpha = 1$, that the rotatory strength of the bis complex equals half the rotatory strength of the tris complex, and that the signs of the transitions can be treated according to exciton theory) gives agreement that a plot of (% by k_1)/(% inverted) *vs.* 1/[CN$^-$] should give a straight line with

$$\text{intercept} = k_1/(k_{\text{inv}} - k_{\text{ret}}) \tag{6}$$

and

$$\text{slope} = k_1 k_{\text{ar}}/k_{\text{di}}(k_{\text{inv}} - k_{\text{ret}}) \tag{7}$$

The derivation is given in Appendix I. The specific rate constants for k_{inv} and k_{ret} are given in Table V along with their activation parameters. The $k_{\text{ar}}/k_{\text{di}}$ ratios obtained from the slopes divided by the intercepts are as follows at various temperatures: 0.5°, 1.35 ± 0.15; 8.0°, 1.09 ± 0.17; 15.0°, 1.35 ± 0.27. The constancy near unity indicates true competing reactions with similar temperature coefficients and constitutes further support for this mechanism. Both reactions 4 and 5 are expected to be rapid. The racemization of the aquocyano complex should be fast because of the weak field of coordinated water, and cyanide is known to displace water from a cobalt(II) complex around 5000 times the rate of water exchange.[14]

This treatment assumes complete retention of configuration for the subsequent anation reaction by the second cyanide ion. Some stereochemical change during the anation will change the absolute value of the numbers but will not effect the overall interpretation. A similar situation exists if the rotatory strength of the bis complex is not exactly half that of the tris complex, as was discussed before.[2] The third assumption of exciton theory signs is dealt with in more detail below.

The trends in the per cent of inverted product *vs.* temperature are definitely outside of experimental error, except for the low cyanide ion concentrations. The breakdown of these trends into inversion and retention paths gives parameters just outside of experimental error, which is indicative (but not conclusive proof) of two activation processes. Assuming these differences are real, the observed activation parameter differences are quite logical. If the inversion path is a result of the displacement of the trans phen ligand [either path (a) or path (b) in Figure 2],[15] then the displacement of either of the cis ligands should give a retained configuration [path (c) in the Figure 2]. As noted previously,[2] electronic perturbation by the cyanide nucleophile would be such as to loosen

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(14) J. P. Jones and D. W. Margerum, *Inorg. Chem.*, 8, 1486 (1969).

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

Temp, °C	k_0,[b] sec^{-1}	k_0,[c] sec^{-1}	k_1, M^{-1} sec^{-1}	Linear corr coeff
0.5	9.10 (0.01) × 10^{-6}	9.10 (0.01) × 10^{-6}	1.85 (0.01) × 10^{-4} [d]	0.9983
8.0	3.20 (0.11) × 10^{-5}	3.21 (0.10) × 10^{-5}	5.65 (0.05) × 10^{-4}	0.9987
15.0	1.00 (0.03) × 10^{-4}	0.98 (0.03) × 10^{-4}	1.66 (0.02) × 10^{-3}	0.9994

[a] Ionic strength 2.00 *M*; subscripts on *k* indicate order in cyanide; *cf.* ref 2, 6; numbers in parentheses are standard deviations. Full data, standard deviations, and per cent error from least-squares fits of the data are available in Appendix III (see paragraph at end of paper regarding supplementary material). [b] Values based on racemization experiments. [c] Values based on intercepts of weighted least-squares linear analysis of cyanide dependence. [d] Unweighted least-squares value of 1.80 (0.04) × 10^{-4} M^{-1} sec^{-1} reported in ref 2.

Table II. Per Cent Optical Inversion for the Reaction of Λ-Fe(phen)$_3{}^{2+}$ with Aqueous Cyanide as a Function of Temperature[a]

[CN$^-$], *M*	0.5°	8.0°	15.0°
0.40	4.92 (0.87)	5.27 (0.64)	3.84 (0.51)
0.60	7.17 (0.36)	6.83 (0.70)	5.44 (0.45)
0.80	9.18 (0.35)	8.37 (0.54)	6.96 (0.38)
1.00	10.3 (0.42)	8.98 (0.41)	8.07 (0.39)
1.49	13.0 (0.35)[b]	11.5 (0.61)	9.80 (0.65)
1.99	14.9 (0.36)	13.3 (0.44)	11.6 (0.75)

[a] Calculations based on two independent calculations using 285 and 310 nm as reference points using triplicate spectra; two independent experiments at each concentration and temperature except as noted. [b] One experiment.

Table III. Least-Squares Fit of (% by k_1)/(% inverted) *vs.* 1/[CN$^-$]

1/[CN$^-$], M^{-1}	% by k_1	% inv	(% by k_1)/(% inv) Exptl	(% by k_1)/(% inv) Calcd
0.5°				
2.52	89.0 (0.96)	4.92 (0.87)	18.1 (3.2)	17.1
1.68	92.4 (1.0)	7.17 (0.36)	12.9 (1.4)	12.7
1.26	94.2 (1.1)	9.18 (0.35)	10.3 (0.41)	10.5
1.00	95.3 (1.1)	10.3 (0.42)	9.25 (0.39)	9.15
0.671	96.8 (1.1)	13.0 (0.35)	7.45 (0.22)	7.43
0.503	97.6 (1.1)	14.9 (0.36)	6.55 (0.18)	6.55
intercept 3.93 (0.31), slope 5.22 (0.40), linear corr coeff 0.999				
8.0°				
2.52	87.5 (1.3)	5.27 (0.64)	16.6 (2.0)	17.9
1.68	91.3 (1.4)	6.83 (0.70)	13.4 (1.4)	13.6
1.26	93.3 (1.5)	8.37 (0.54)	11.2 (0.74)	11.4
1.00	94.6 (1.5)	8.98 (0.41)	10.5 (0.51)	10.0
0.671	96.3 (1.5)	11.5 (0.61)	8.38 (0.46)	8.30
0.503	97.2 (1.5)	13.3 (0.44)	7.31 (0.27)	7.42
intercept 4.80 (0.47), slope 5.21 (0.60), linear corr coeff 0.988				
15.0°				
2.52	86.8 (1.5)	3.84 (0.51)	22.6 (3.0)	22.1
1.68	90.8 (1.6)	5.44 (0.45)	16.7 (1.4)	16.4
1.26	92.9 (1.6)	6.96 (0.38)	13.4 (0.76)	13.5
1.00	94.3 (1.6)	8.07 (0.39)	11.7 (0.60)	11.8
0.671	96.1 (1.7)	9.80 (0.65)	9.81 (0.67)	9.56
0.503	97.1 (1.7)	11.6 (0.75)	8.37 (0.56)	8.42
intercept 5.01 (0.78), slope 6.78 (0.83), linear corr coeff 0.998				

Table IV. Effect of Hydroxide Ion on the Λ-Fe(phen)$_3{}^{2+}$–Cyanide Inversion at 0.0°

[CN$^-$], *M*	10^3 × [OH$^-$],[a] *M*	% inversion	[CN$^-$], *M*	10^3 × [OH$^-$],[b] *M*	% inversion
0.39	2.6	4.1 (0.4)	0.39	6	3.5 (0.1)
0.58	3.1	7.1 (0.4)	0.58	6	6.5 (0.4)
0.77	3.6	8.7 (1.4)	0.77	6	8.3 (0.4)
0.97	4.1	10.5 (0.4)	0.97	6	9.8 (0.4)
1.93	5.7	15.0 (0.5)	1.93	6	15.0 (0.5)

[a] Calculated from hydrolysis ($K_H = 1.7 \times 10^{-5}$). [b] Measured with pH meter after adjustment.

both ends of the trans ligand while primarily loosening only one end of the cis ligands. The activation parameters are consistent with this evaluation; *i.e.*, the activation energy (E_a) for the inversion path (23.2 kcal/mol) is lowered more from the first-order dissociation path value (29.9 kcal/mol)[16] than is the retention path activation energy (24.5 kcal/mol). The activation energy for the inversion path mirrors the effect of the cyanide perturbation on the trans ligand and the activation energy for the retention path mirrors the lower perturbation on the cis ligand. The lower frequency factor for the inversion path is also consistent with the low probability of producing the concerted effort necessary for the inversion; *i.e.*, the rotation of one ligand concurrent with the displacement of another one. The retention requires only the displacement.

The majority of the product appears racemic because equal amounts of inverted and retained product from the two paths give no net rotation. Furthermore, part of the intermediate aquocyano species racemizes prior to substitution by the second cyanide ion.

2. Inversion–Racemization Mechanism. Another mechanism which fits the (% by k_1)/(% inverted) *vs.* 1/[CN$^-$] plot being a straight line is illustrated by eq 8–11; only the reactions for the Δ isomer are shown.

$$\Delta\text{-Fe(phen)}_3{}^{2+} + \text{CN}^- \xrightarrow{k_{1_i}} \Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{phen} \qquad (8)$$

$$\Delta\text{-Fe(phen)}_3{}^{+} + \text{CN}^- \xrightarrow{k_{1_r}} rac\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{phen} \qquad (9)$$

$$\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ + \text{CN}^- \xrightarrow{k_{\text{di}}} \Delta\text{-Fe(phen)}_2(\text{CN})_2 + \text{H}_2\text{O} \qquad (10)$$

$$\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ \xrightarrow{k_{\text{ar}}} rac\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+ \qquad (11)$$

The same assumptions of 100% retained anation, 50% rotatory strength for the product, and configuration by exciton theory are used to yield

$$\text{intercept} = k_1/k_{1_i} \qquad (12)$$

and

$$\text{slope} = k_1 k_{\text{ar}}/k_{1_i} k_{\text{di}} \qquad (13)$$

as detailed in Appendix II. The specific rate constants and the activation parameters obtained for this mechanism are given in Table V. Although this mechanism was suggested as possible in our initial investigation,[2] a consideration of the figure and/or molecular models makes it difficult to envision racemization through loss of a cis ligand if the more con-

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(15) Molecular models show that the CN$^-$ must enter on or very near a C_2 axis edge, which effectively gives one trans phen and two cis phen ligands. The perturbational and stereochemical arguments are unchanged if the cyanide is not exactly on the edge. With regard to path (a), E. D. McKenzie, *Coord. Chem. Rev.*, 6, 187 (1971), has reviewed suggestions of similar (phen)$_2$ with trans configurations and concluded that they are nonexistent because of ligand overlap in the 2 and 9 positions. Therefore, a* is not a symmetrical trans species because N$_a$ cannot bond because of steric repulsions. Furthermore, N$_a$ cannot go back to its original position now occupied by cyanide; therefore, it must bond at the position of N$_c$ giving inversion. *Cf.* L. H. Berka, W. T. Edwards, and P. A. Christian, *Inorg. Nucl. Chem. Lett.*, 7, 265 (1971).

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

		Inversion–retention mechanism		Inversion–racemization mechanism	
	Overall k_1	k_{inv}	k_{ret}	k_{1_i}	k_{1_r}
$k(0.5°), M^{-1}\ sec^{-1}$	1.85 (0.01) × 10^{-4}	1.16 (0.04) × 10^{-4}	6.90 (0.40) × 10^{-5}	4.71 (0.37) × 10^{-5}	1.38 (0.04) × 10^{-4}
$k(8.0°), M^{-1}\ sec^{-1}$	5.65 (0.05) × 10^{-4}	3.41 (0.13) × 10^{-4}	2.24 (0.14) × 10^{-4}	1.18 (0.12) × 10^{-4}	4.47 (0.12) × 10^{-4}
$k(15.0°), M^{-1}\ sec^{-1}$	1.66 (0.02) × 10^{-3}	9.96 (0.56) × 10^{-4}	6.64 (0.59) × 10^{-4}	3.31 (0.52) × 10^{-4}	1.33 (0.06) × 10^{-3}
E_a, kcal/mol	23.7 (0.6)	23.2 (0.8)	24.5 (0.3)	21.0 (1.4)	24.5 (0.3)
ln A (A in $M^{-1}\ sec^{-1}$)	35.0 (1.0)	33.6 (1.4)	35.4 (0.5)	28.7 (2.6)	36.1 (0.6)
Linear corr coeff	0.9997	0.9995	0.9999	0.9977	0.9999
$\Delta H^{\ddagger}$, kcal/mol	23.1 (0.6)	22.6 (0.8)	23.9 (0.3)	20.4 (1.4)	23.9 (0.3)
$\Delta S^{\ddagger}$, eu	9.0 (2.0)	6.2 (2.7)	9.8 (1.0)	−3.6 (5.1)	11.2 (1.1)

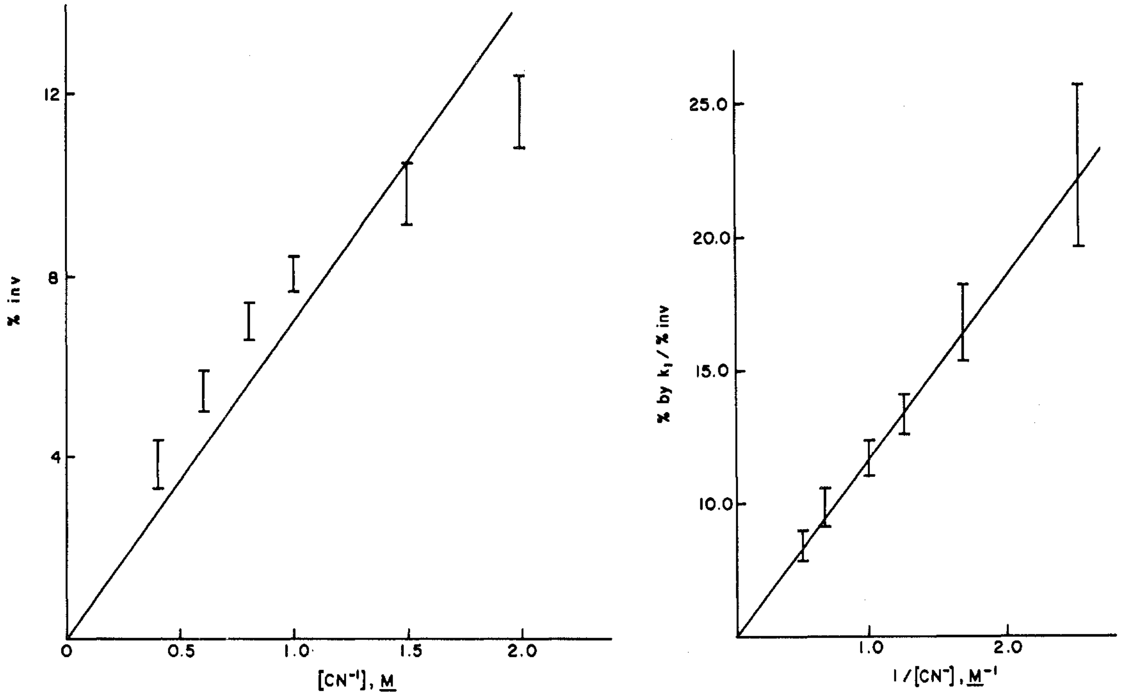

Figure 1. Plots of per cent inversion *vs.* [CN^-] and of (% by k_1/% inv) *vs.* 1/[CN^-] for the aqueous reaction between $Fe(phen)_3{}^{2+}$ and CN^- at 15.0°.

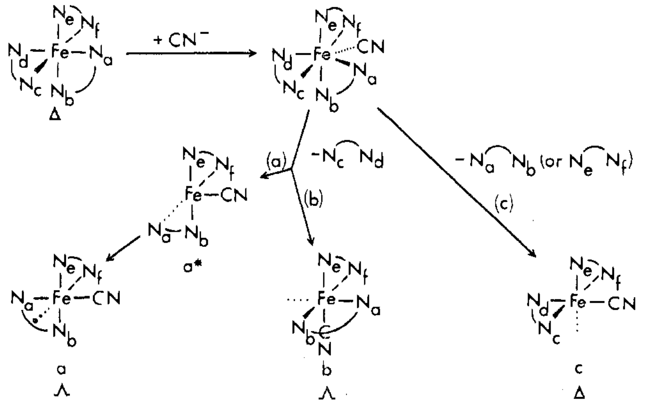

Figure 2. Proposed inversion paths (a) and (b) together with retention path (c) for cyanide acting as a nucleophile on an iron(II)-tris(diimine) complex with rigid ligands such as $Fe(phen)_3{}^{2+}$. Intermediates a, b, and c are assumed to add water and cyanide in the vacant octahedral position (dotted) without further stereochange, although racemization of the aquocyano complex, eq 9, appears to compete with anation. N_a of a* cannot bond because of steric factors.

certed path(s) for trans displacement give a stereospecific inverted product. Therefore, although the inversion–racemization mechanism is mathematically possible, the mechanism is not as logical from a molecular standpoint as is the inversion–retention mechanism.

The activation parameters are logical for such a mechanism, if it were to occur. The activation energy for the inversion path is again lower as anticipated for loss of the trans-labilized chelating ligand, which must occur for inversion to be obtained. Other things being equal, the entropy of activation should be higher for a loose transition state (such as would occur in a racemization path) than for a concerted, stereospecific reaction. Alternatively, the lower probability of a concerted process can be used as in the preferred mechanism discussed above. Therefore, whereas the appropriate activation parameters have been obtained, the agreement does not constitute proof of the inversion–racemization mechanism because the mechanism is not as logical chemically as the inversion–retention mechanism noted above. Furthermore, the activation parameters for both of the preceding mechanisms are consistent with the concept that the optical inversion is a true chemical inversion as suggested originally through exciton theory arguments.[2] Naturally, other factors, such as differing solvent reorganization in the transition states, could negate the above activation arguments, but the correlation between the stereochemistry and the activation parameters is reassuring. Studies with other related systems are needed to prove the generality of the correlation between entropies of activation and inversion in associative octahedral reactions.

3. Hydroxide Intervention Mechanism. Although the per cent inverted product obtained at 0.5° is reasonably proportional to the hydroxide ion concentration,[17] the fits at 8.0 and 15.0° are much less satisfactory than the 1/[CN$^-$] relationship noted above. Furthermore, as is noted in Table IV, a significant increase in the hydroxide ion concentration does not increase the amount of inverted products. In fact, a slight decrease is observed. This small decrease is probably the result of the hydroxide reaction[6,18] with traces of oxygen.[19] The hydroxide intermediate would have a lower field than the cyano intermediate; therefore, complete racemization is logical for any hydroxide substitution. Therefore, the role of hydroxide is minimal under our reaction conditions. Qualitative experiments in air have shown appreciably lower inversion percentages, apparently because of the hydroxide oxygen complication noted by Nord and Pizzino.[19]

4. Retention Predominance Mechanisms. What if the exciton theory assignments for the dicyano product lead to the wrong configuration? The retention path would then predominate and the activation parameters associated with the inversion specific rate constants (Table V) would be associated with retention paths. Considering the retention-inversion pair, the activation energy of the retained path would have to be lower than the activation energy of the inversion path—in opposition to the direction suggested for cyanide perturbation earlier.[2] Furthermore, the preexponential term for an associative reaction yielding retention should be larger than a concerted inverted process as noted above. For the retention–racemization pair the activation energy situation is identical with the retention–inversion pair; however, a loose transition state for racemization does agree with the observed entropies of activation. Therefore, in general the activation parameters are less satisfactory for retention-predominating mechanisms than for the inversion-predominating mechanisms discussed above. In other words, the observed activation parameters provide support for exciton theory spectral assignments for these species.

Furthermore, the exciton model for these complexes appears to give the appropriate signs and energies correctly. Whereas anomalous energy level shifts (as measured by absorption spectroscopy) might cause incorrect assignments of circular dichroism bands by exciton theory,[20] this Fe(II)-phen series has a regular spectral shift.[2] Vibronic coupling might also alter the assignments,[20] but the circular dichroism spectra for the iron(II) α-diimines at 80°K exhibit no vibrational structure, which further supports the use of simple exciton theory.[21] Recent molecular orbital calculations on these iron(II) systems[22] concur with the original exciton theory assignments as do intermediate exciton-coupling calculations.[21,23] Results of a gaussian band shape analysis for correlated circular dichroism and magnetic circular dichroism spectra[24] also concur with Sanders'[22d] assignments for the $Fe(phen)_3^{2+}$ ion. Finally, Gillard, Hill, and Maskill[25] have chemically correlated the phen and bipy series for ruthenium and have found agreement with exciton theory. We have much greater faith in inversions based on configurations related by exciton theory than in inversions based on d–d CD correlations. The problems with d–d correlations have been amply documented recently by Bosnich,[26] although theoretical progress is being made.[27]

5. Other Mechanisms. Naturally the possibility exists that retention, inversion, and racemization all occur as basic steps. No evidence has been found to add this complication, but racemization of the "pseudo-trans" species a* together with inversion *via* path (b) and retention *via* path (c) appears possible at first glance. We anticipate that a* should lose the N_a-N_b phen to produce $Fe(phen)(CN)_4^{2-}$, at least part of the time, if that phen ligand is mobile enough to give equivalence like a trans complex, considering the steric repulsions.[15] Neither we nor Margerum and Morgenthaler[6] have found any evidence for any of the tetracyano complexes under normal temperatures. In the absence of stereochemical labels to distinguish between paths (a) and (b), this complication is not considered further herein but awaits experiments with unsymmetrical diimines.

The specific rate constants for the ion multiplet paths noted in ref 2 have not been evaluated. The necessity of large equilibrium constants in water for the ion triplets[2] makes this mathematical exercise unwarranted.

6. Conclusion. The inversion–retention mechanism is the most logical mechanism consistent with all experimental and theoretical considerations. The close proximity of states with unpaired electrons in the iron(II) system apparently allows nucleophiles such as cyanide significantly to perturb the spin-paired ground state.[2,5] Once cyanide is close enough to perturb the phen complex, the perturbation forces phen to leave. Whether a spin change occurs is still speculative but is in agreement with activation parameters observed. Spees, Perumareddi, and Adamson[28] have shown that whereas spin-paired d^6 pentagonal bipyramids should have high activation energies (see ref 5), d^6 pentagonal bipyramids with unpaired spins could have activation energies in the same range as the normal dissociative spin-paired d^6 systems as postulated by Archer[29] for cobalt(III) inversions earlier. A rapid repairing must occur; otherwise the aquocyano racemization would completely predominate the reaction. Placement of an electron in the $d_{x^2-y^2}$ orbital (using N_e-Fe-N_b in Figure 2 as the z axis) without a change in spin would be sufficient to cause the inversion, but a much higher activation energy should be required.[28]

7. Related Studies. Kinetic studies by Burgess and coworkers[30] with racemic $Fe(bipy)_3^{2+}$ and $Fe(PBA)_3^{2+}$ indicate activation parameters for the k_1 cyanide-dependent path analogous to our results as indicated in Table VI. The earlier values on the $Fe(phen)_3^{2+}$ system[6] were determined from data with considerable scatter in the data and extrapolation of our values to the higher temperatures suggest the dif-

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Table VI. Related Activation Parameters for Cyanide-Dependent Reactions with Iron(II) Chelates

Iron substrate	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
$Fe(phen)_3^{2+}$	20 (3)	−3	6
	20.5 (2.8)	−1.6 (9.4)	6[a]
	23.7 (0.6)	9.0 (2.0)	This study
$Fe(bipy)_3^{2+}$	23.0 (0.8)	9	30b
$Fe(PBA)_3^{2+}$	20.4	10	30a

[a] Recalculated from ref 6 raw data applying calculation refinements of this study.

ferences are largely a result of the large experimental error in the earlier study.

Even though the overall k_1 term has similar activation parameters, the intimate look at the breakdown of the cyano-activated complex may reveal significant differences with more flexible ligands such as bipy. For example, unidentate bipy is evident in the substitution kinetics of $Fe(bipy)_3^{2+}$, whereas with $Fe(phen)_3^{2+}$ this complication does not occur.[5] That is, unidentate phen is possible in the addition and loss of the first such ligand in octahedral species but is sterically unlikely for tris species. Investigation of the reaction between $Fe(bipy)_3^{2+}$ and cyanide indicates a predominance of *retained* product with an *increase* in the per cent retained as the temperature increases.[24] Here again the inversion path appears to have a lower $\Delta S^{\ddagger}$ than the retention path (2.4 *vs.* 6.8 eu) consistent with the above arguments.

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Appendix I

For the retention plus inversion mechanism of the Λ-$Fe(phen)_3^{2+}$ isomer reacting with cyanide (eq 2-5) the steady-state assumption for the Λ-$Fe(phen)_2(H_2O)(CN)^+$ species is

$$\frac{d[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]}{dt} = k_{\text{ret}}[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] + {}^*\frac{k_{\text{ar}}}{2}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - \frac{k_{\text{ar}}}{2}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - k_{\text{di}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] = 0 \quad \text{(I-1)}$$

with an analogous expression for the Δ isomer. The asterisked term for the Λ isomer contains the Δ isomer which can be related to the Λ isomer through the amount of total aquocyano species

$$d[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]/dt = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] - k_{\text{di}}[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \quad \text{(I-2)}$$

Again using the steady-state approximation, rearrangement gives

$$[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}]/k_{\text{di}} \quad \text{(I-3)}$$

Because

$$\frac{k_{\text{ar}}}{2}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{k_{\text{ar}}}{2}\{[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - [\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]\} \quad \text{(I-4)}$$

from (I-3) the asterisked term in (I-1) is thus equal to

$$\frac{k_{\text{ar}}}{2}\left[\frac{k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}]}{k_{\text{di}}}\right] - \frac{k_{\text{ar}}}{2}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] \quad \text{(I-5)}$$

Rearranging

$$[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{\left(k_{\text{ret}}[\text{CN}^-] + \dfrac{k_{\text{ar}}k_1}{2k_{\text{di}}}\right)[\Lambda\text{-Fe(phen)}_3{}^{2+}]}{k_{\text{ar}} + k_{\text{di}}[\text{CN}^-]} \quad \text{(I-6)}$$

Similarly

$$[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{(k_{\text{inv}}[\text{CN}^-] + k_1k_{\text{ar}}/2k_{\text{di}})[\Lambda\text{-Fe(phen)}_3{}^{2+}]}{k_{\text{ar}} + k_{\text{di}}[\text{CN}^-]} \quad \text{(I-7)}$$

As a check, (I-6) and (I-7) can be added together to give (I-3) using the relationship $k_1 = k_{\text{ret}} + k_{\text{inv}}$ and rearranging as

$$\left(\frac{k_1[\text{CN}^-] + k_{\text{ar}}k_1/k_{\text{di}}}{k_{\text{di}}[\text{CN}^-] + k_{\text{ar}}}\right)[\Lambda\text{-Fe(phen)}_3{}^{2+}] = \frac{k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}]}{k_{\text{di}}} \quad \text{(I-8)}$$

Furthermore, if $\alpha = 1$ in eq 5, then for the k_1 path

$$\frac{d[\Delta\text{-Fe(phen)}_2(\text{CN})_2]}{dt} = k_{\text{di}}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \quad \text{(I-9)}$$

$$\frac{d[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{dt} = k_{\text{di}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \quad \text{(I-10)}$$

$$\frac{d[\text{total Fe(phen)}_2(\text{CN})_2]}{dt} = k_{\text{di}}[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \quad \text{(I-11)}$$

and substitution of the steady-state concentration values from (I-6), (I-7), and (I-3) into (I-10), (I-9), and (I-11), respectively, yields the expressions

$$\frac{d[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{dt} = k_{\text{di}}\left(\frac{k_{\text{ret}}[\text{CN}^-] + k_{\text{ar}}k_1/2k_{\text{di}}}{k_{\text{ar}} + k_{\text{di}}[\text{CN}^-]}\right)[\Lambda\text{-Fe(phen)}_3{}^{2+}] \times [\text{CN}^-] \quad \text{(I-12)}$$

which rearranges to give

$$\frac{\mathrm{d}[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{\mathrm{d}t} = \left(\frac{{}^1\!/_2 k_1 k_{\mathrm{ar}} + k_{\mathrm{ret}} k_{\mathrm{di}}[\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]}\right)[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] \qquad \text{(I-13)}$$

Similarly

$$\frac{\mathrm{d}[\Delta\text{-Fe(phen)}_2(\text{CN})_2]}{\mathrm{d}t} = \left(\frac{{}^1\!/_2 k_1 k_{\mathrm{ar}} + k_{\mathrm{inv}} k_{\mathrm{di}}[\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]}\right)[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] \qquad \text{(I-14)}$$

And the total rate by the k_1 route is

$$\mathrm{d}[\text{total Fe(phen)}_2(\text{CN})_2]/\mathrm{d}t = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] \qquad \text{(I-15)}$$

where (I-13) plus (I-14) is identical with (I-15), as expected.

The product distribution obtained from the reaction will be in proportion to the rates of the individual paths. That is, the per cent by k_1 for the mechanism under consideration will be equal to (I-13) plus (I-14) divided by the sum of the rates for both the k_0 and k_1 terms, whereas the observable per cent inversion will be (I-14) minus (I-13) divided by the sum of both the k_0 and k_1 terms. The ratio of (% by k_1)/(% inverted) then allows a cancelation of the denominators in the eq I-13 and I-14, the $[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]$ term, and the sum of rates noted in the preceding sentence. That is

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = \frac{k_1 k_{\mathrm{ar}} + k_{\mathrm{ret}} k_{\mathrm{di}}[\text{CN}^-] + k_{\mathrm{inv}} k_{\mathrm{di}}[\text{CN}^-]}{k_{\mathrm{inv}} k_{\mathrm{di}}[\text{CN}^-] - k_{\mathrm{ret}} k_{\mathrm{di}}[\text{CN}^-]} \qquad \text{(I-16)}$$

Rearranging (and canceling $k_{\mathrm{di}}[\text{CN}^-]$ in what becomes the second term) yields

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = \frac{k_1 k_{\mathrm{ar}}}{(k_{\mathrm{inv}} - k_{\mathrm{ret}})k_{\mathrm{di}}[\text{CN}^-]} + \frac{k_{\mathrm{ret}} + k_{\mathrm{inv}}}{k_{\mathrm{inv}} - k_{\mathrm{ret}}} \qquad \text{(I-17)}$$

But $k_{\mathrm{ret}} + k_{\mathrm{inv}} = k_1$ so

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = \frac{k_1}{k_{\mathrm{inv}} - k_{\mathrm{ret}}} + \frac{k_1 k_{\mathrm{ar}}}{(k_{\mathrm{inv}} - k_{\mathrm{ret}})k_{\mathrm{di}}[\text{CN}^-]} \qquad \text{(I-18)}$$

Therefore a plot of (% by k_1)/(% inverted) *vs.* $1/[\text{CN}^-]$ has an intercept of $k_1/(k_{\mathrm{inv}} - k_{\mathrm{ret}})$ and a slope of $k_1 k_{\mathrm{ar}}/(k_{\mathrm{inv}} - k_{\mathrm{ret}})k_{\mathrm{di}}$.

Appendix II

The inversion plus racemization mechanistic possibility (eq 8 to 11) for the reaction of optically active $\text{Fe(phen)}_3{}^{2+}$ with cyanide without detection of the aquocyano intermediate suggests the use of the steady-state assumption for the $\text{Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+$ species. For the $\Lambda\text{-Fe(phen)}_3{}^{2+}$ ion used herein

$$\begin{aligned}\mathrm{d}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]/\mathrm{d}t = {} & (k_{1_{\mathrm{i}}} + {}^1\!/_2 k_{1_{\mathrm{r}}})[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] + \\ & {}^1\!/_2 k_{\mathrm{ar}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - \\ & {}^1\!/_2 k_{\mathrm{ar}}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - \\ & k_{\mathrm{di}}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] = 0 \qquad \text{(II-1)}\end{aligned}$$

$$\begin{aligned}\mathrm{d}[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]/\mathrm{d}t = {} & k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] - \\ & k_{\mathrm{di}}[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] = 0 \qquad \text{(II-2)}\end{aligned}$$

which rearranges to

$$[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}]/k_{\mathrm{di}} \qquad \text{(II-3)}$$

Replacing $[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]$ in (II-1) by $[\text{total Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - [\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]$, substituting the (II-3) relationship for the total aquocyano concentration, and rearranging give

$$[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{(k_{1_{\mathrm{i}}} + {}^1\!/_2 k_{1_{\mathrm{r}}})[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} + \frac{{}^1\!/_2 k_{\mathrm{ar}} k_1[\text{Fe(phen)}_3{}^{2+}]}{k_{\mathrm{di}}(k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-])} \qquad \text{(II-4)}$$

Assuming the anation gives complete retention

$$\mathrm{d}[\Delta\text{-Fe(phen)}_2(\text{CN})_2]/\mathrm{d}t = k_{\mathrm{di}}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \qquad \text{(II-5)}$$

Substituting (II-4) into (II-5) gives

$$\frac{\mathrm{d}[\Delta\text{-Fe(phen)}_2(\text{CN})_2]}{\mathrm{d}t} = \frac{k_{\mathrm{di}}(k_{1_{\mathrm{i}}} + {}^1\!/_2 k_{1_{\mathrm{r}}})[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]^2}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} + \frac{{}^1\!/_2 k_{\mathrm{ar}} k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} \qquad \text{(II-6)}$$

The Λ isomer can be evaluated similarly

$$\begin{aligned}\mathrm{d}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+]/\mathrm{d}t = {} & {}^1\!/_2 k_{1_{\mathrm{r}}}[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] + \\ & {}^1\!/_2 k_{\mathrm{ar}}[\Delta\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - \\ & {}^1\!/_2 k_{\mathrm{ar}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] - \\ & k_{\mathrm{di}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] = 0 \qquad \text{(II-7)}\end{aligned}$$

which can be converted to

$$[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+] = \frac{{}^1\!/_2 k_{1_{\mathrm{r}}}(\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} + \frac{{}^1\!/_2 k_{\mathrm{ar}} k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}]}{k_{\mathrm{di}}(k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-])} \qquad \text{(II-8)}$$

and for the anation of the Λ ion

$$\mathrm{d}[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]/\mathrm{d}t = k_{\mathrm{di}}[\Lambda\text{-Fe(phen)}_2(\text{H}_2\text{O})(\text{CN})^+][\text{CN}^-] \qquad \text{(II-9)}$$

or by substitution of (II-8) in (II-9)

$$\frac{\mathrm{d}[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{\mathrm{d}t} = \frac{k_{\mathrm{di}}({}^1\!/_2 k_{1_{\mathrm{r}}})[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]^2}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} + \frac{{}^1\!/_2 k_{\mathrm{ar}} k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]}{k_{\mathrm{ar}} + k_{\mathrm{di}}[\text{CN}^-]} \qquad \text{(II-10)}$$

Furthermore, (II-6) plus (II-10) gives the total rate by k_1 or

$$d[\text{total Fe(phen)}_2(\text{CN})_2]/dt = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] \qquad \text{(II-11)}$$

The product distribution will be in proportion to the rates of the species. That is, the total by k_1 will be (II-11) divided by the sum of the k_0 and k_1 rates. The observable per cent inverted will be the difference in the Δ and Λ isomer production through the k_1 path [(II-6)-(II-10)] divided by the sum of the k_0 and k_1 rates. Therefore, the (% by k_1)/(% inverted) ratio eliminates the rate sums (through cancelation) and is equal to

$$\frac{d[\text{total Fe(phen)}_2(\text{CN})_2]}{dt} \Bigg/ \left(\frac{d[\Delta\text{-Fe(phen)}_2(\text{CN})_2]}{dt} - \frac{d[\Lambda\text{-Fe(phen)}_2(\text{CN})_2]}{dt}\right) = k_1[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-] \Bigg/ \left(\frac{k_{\text{di}}k_{1_\text{r}}[\Lambda\text{-Fe(phen)}_3{}^{2+}][\text{CN}^-]^2}{k_{\text{ar}} + k_{\text{di}}[\text{CN}^-]}\right) \qquad \text{(II-12)}$$

Canceling and rearranging give

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = \frac{k_1(k_{\text{ar}} + k_{\text{di}}[\text{CN}^-])}{k_{\text{di}}k_{1_\text{i}}[\text{CN}^-]} \qquad \text{(II-13)}$$

which is equivalent to eq 18 of ref 2, keeping in mind that $k_1 = k_{1_\text{i}} + k_{1_\text{r}}$. Further rearrangement gives

$$\frac{\%\text{ by }k_1}{\%\text{ inverted}} = \frac{k_1}{k_{1_\text{i}}} + \frac{k_1k_{\text{ar}}}{k_{1_\text{i}}k_{\text{di}}[\text{CN}^-]} \qquad \text{(II-14)}$$

so that a plot of (% by k_1)/(% inverted) *vs.* $1/[\text{CN}^-]$ has an intercept of k_1/k_{1_i} (or as given in ref 2: $1 + k_{1_\text{r}}/k_{1_\text{i}}$) and a slope of $k_1k_{\text{ar}}/k_{1_\text{i}}k_{\text{di}}$.

Registry No. Λ-[Fe(phen)$_3$](ClO$_4$)$_2$, 51174-98-2; CN$^-$, 57-12-5.

Supplementary Material Available. Appendix III, showing the data used for determining specific rate constants for the reaction of aqueous Fe(o-phen)$_3{}^{2+}$ with cyanide, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1551.

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Reaction of Iron(III) Tris(xanthates) and Tris(dithiophosphinates) with Pyridine

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The reaction of pyridine with tris(O-methyl xanthato)iron(III), tris(O-ethyl xanthato)iron(III), tris(diphenyl dithiophosphinato)iron(III), and tris(dicyclohexyl dithiophosphinato)iron(III) leads to bright yellow complexes which have magnetic moments of 4.9-5.0 BM, isomer shifts of 1.2 mm/sec, and large quadrupole splittings of ~3 mm/sec at room temperature. Such values are strongly indicative of iron(II) complexes. From conductometry and infrared data, these adducts are most likely dipyridinobis(xanthato or dithiophosphinato)iron(II) complexes.

Introduction

Almost 60 years ago, Dubsky, *et. al.*, reported that tris(O-ethyl xanthato)iron(III)[1] and tris(O-methyl xanthato)iron(III)[2] form golden yellow, crystalline 1:3 adducts, of limited stability, with pyridine. Various structures have been proposed for these adducts, including those with pyridine coordinated to the iron(III)[3] and monodentate xanthate and with pyridine forming a kind of semipolar bond with the carbon atom in bidentate xanthate.[3] None of the proposed structures is really satisfactory. Because of our interest in iron complexes with bidentate sulfur ligands[4-6] we have investigated these adducts and similar ones of iron(III) tris(dithiophosphinates), using Mossbauer spectroscopy, magnetic susceptibility measurements, conductivity measurements, and infrared spectroscopy, and have found that they are most likely complexes of iron(II).

Experimental Section[7]

Unless otherwise indicated all starting materials and solvents were reagent grade. Ferric methyl and ethyl xanthates, [Fe(Me(xn))$_3$] and [Fe(Et(xn))$_3$], were prepared from aqueous solutions of ferric nitrate and the potassium xanthate and were recrystallized several times from benzene-cyclohexane mixtures. These complexes were used within 3 days after preparation. Ferric tris(dithiophosphinates), [Fe(R$_2$PS$_2$)$_3$], R = C$_6$H$_5$ and C$_6$H$_{11}$, were prepared by mixing solutions of anhydrous ferric chloride and diphenyldithiophosphinic acid (Practical grade, Aldrich Chemical Co. and K and K Chemical Co.) or ammonium dicyclohexyl dithiophosphinate (Aldrich Chemical Co.) and recrystallizing the precipitates from methylene chloride-ethanol mixtures.

Anal. Calcd for [Fe(Ph$_2$dtp)$_3$]: C, 53.79; H, 3.76; S, 23.93. Found: C, 54.02; H, 3.77; S, 23.74 (Galbraith Laboratories, Knoxville, Tenn.). Calcd for [Fe(c-Hx$_2$dtp)$_3$]: C, 51.47; H, 7.92; P, 10.95. Found: C, 51.82; H, 8.02; P, 9.33 (Chemalytics Inc., Tempe, Ariz.).

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[7] Abbreviations used: Me, CH$_3$; Et, C$_2$H$_5$; Ph, C$_6$H$_5$; c-Hx, C$_6$H$_{11}$; Rxn, ROCS$_2^-$; R$_2$dtp, R$_2$PS$_2^-$.