Kinetic Investigation of Carbon–Nitrogen Bond Rotation in Dithiocarbamato Complexes of Iron by Proton Magnetic Resonance

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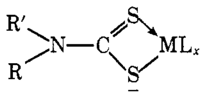
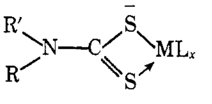
Abstract: Complexes of the types $\mathrm{Fe^{II}(dtc)_2phen}$, -bipy, $\mathrm{Fe^{III}(dtc)_3}$, and $\mathrm{[Fe^{IV}(dtc)_3]BF_4}$, where dtc is an N,N-disubstituted dithiocarbamate, have been prepared and their barriers to $\mathrm{S_2C\overset{...}{-}N}$ bond rotation measured by total line-shape analyses of their pmr spectra in $\mathrm{CD_2Cl_2}$ solution. The kinetic parameters are greatly dependent on the formal oxidation state of iron. $\Delta F^{\ddagger}(298°)$ values are *ca.* 8.6, 12.0, and 15.0 kcal/mol for $\mathrm{Fe^{II}}$, $\mathrm{Fe^{III}}$, and $\mathrm{Fe^{IV}}$ complexes, respectively. This trend is interpreted in terms of increased Fe–S, d_π–d_π back-bonding for the more reduced complexes thereby destabilizing the $\mathrm{S_2{}^{2-}C{=}N^{+}R_2}$ resonance structure and lowering the barrier to $\mathrm{C\overset{...}{-}N}$ bond rotation. No significant dependence on the N substituent was found. *N,N,N′,N′*-Tetramethylthiuram disulfide was also synthesized and subjected to a complete kinetic analysis. The barrier to $\mathrm{C\overset{...}{-}N}$ bond rotation in this compound is similar to those of dtc esters and the $\mathrm{Fe^{IV}}$ complexes.

High barriers to $\mathrm{C\overset{...}{-}N}$ bond rotation in substituted amides, thioamides, carbamates, and thiocarbamates are a characteristic property of this class of compound.[1–4] Numerous kinetic analyses have been performed on these compounds using nmr spectroscopy.[1–5] Controversy has developed regarding the experimental techniques employed because widely scattered activation parameters have been reported by different researchers for the same compound.[3,4] Indeed, the many studies on *N,N*-dimethylformamide alone have yielded activation energies, E_a, ranging from 6.3 to 28.2 kcal/mol.[3] Most of these studies employed approximate methods to analyze the pmr spectra and were performed using early model spectrometers. Recent studies which employ a total line-shape analysis, TLSA, on spectra obtained using highly homogeneous spectrometers yield parameters which are in good agreement.[3] Binsch[3] discusses the general field in a recent review and concludes that analyses employing the TLSA technique are the most reliable. He also points out that the most accurate studies on $\mathrm{C\overset{...}{-}N}$ bond rotation usually yield entropy of activation values, $\Delta S^{\ddagger}$, which are approximately zero.[6]

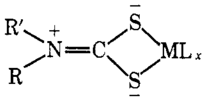
Only several studies on the kinetics of $\mathrm{S_2C\overset{...}{-}N}$ bond rotation in N,N-disubstituted dithiocarbamate, RR′(dtc), compounds have been performed,[7–9] even though numerous reports of hindered rotation have appeared.[10–17] All of these studies employed pmr spectroscopy. Dtc compounds have a characteristic infrared band between *ca.* 1450 and 1550 cm^{-1} which is assigned as the $\mathrm{C\overset{...}{-}N}$ stretching vibration.[18] This frequency range indicates a $\mathrm{C\overset{...}{-}N}$ bond order between one (1250–1350 cm^{-1}) and two (1640–1690 cm^{-1}).[19] X-Ray investigations on numerous dtc compounds show $\mathrm{C\overset{...}{-}N}$ bond lengths of *ca.* 1.29–1.42 Å, which are also consistent with partial double bond character (C—N, ~1.46 and C=N, ~1.27 Å).[20] Chatt, *et al.*,[21] explained this shortened $\mathrm{C\overset{...}{-}N}$ bond in transition metal RR′(dtc) complexes as a result of resonance structures Ia–c. Structure Ic results in a C–N bond order greater than one. It has been qualitatively shown that R groups which are electron donating and L ligands which are electron withdrawing increase the $\mathrm{C\overset{...}{-}N}$ stretching frequency, $\nu(\mathrm{C\overset{...}{-}N})$, presumably by stabilizing Ic.[21–23]



Ia



Ib



Ic

There have been no quantitative $\mathrm{C\overset{...}{-}N}$ bond rotation kinetic studies reported on transition metal–dtc com-

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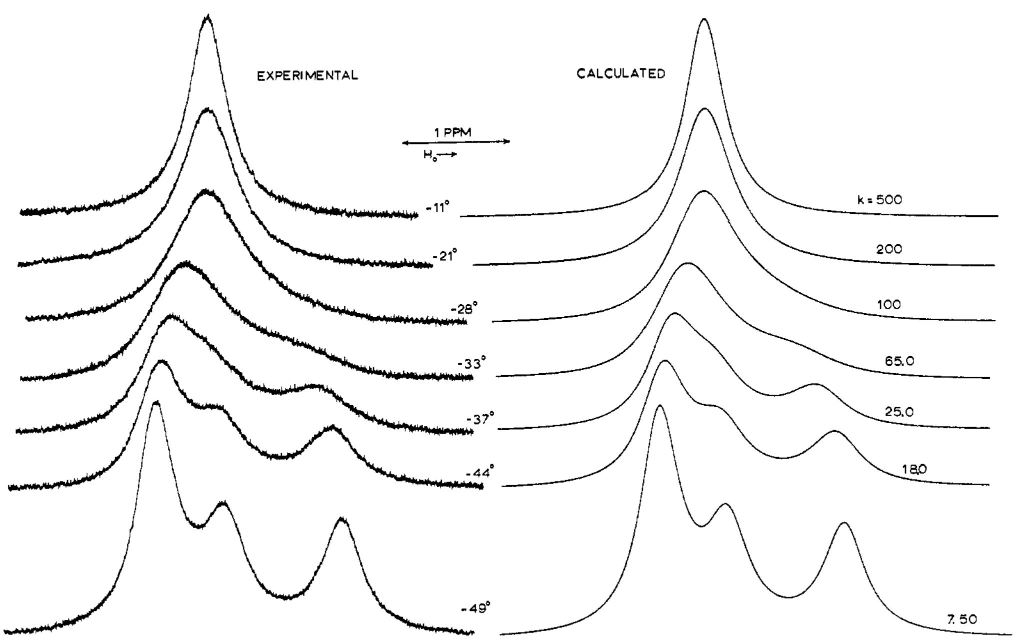

Figure 1. Observed and calculated line shapes for methyl groups of Fe(Me(i-Pr)(dtc))$_3$ in CD_2Cl_2 solution at 100 MHz. Calculated line shapes are for random scrambling and rate constants, k, are in sec^{-1}.

plexes where the oxidation state of the metal has been varied.[24] Studies of this type should yield important information on the type of metal–sulfur bonding in complexes with various d^n electronic configurations. Studies with different ligands, L (defined in I), should also show an electronic effect which would be transmitted through the metal orbitals.

The present work employs a TLSA to measure activation parameters to C$\overset{\cdots}{-}$N bond rotation in a series of paramagnetic iron RR′(dtc) complexes in CD_2Cl_2 solution. The formal oxidation states of iron in these complexes are II, III, and IV. N,N,N',N'-Tetramethylthiuram disulfide, Me$_4$tds, was also subjected to a TLSA. A large variation in activation energy to C$\overset{\cdots}{-}$N bond rotation has been found for these compounds of different oxidation states and is interpreted in terms of iron–sulfur π back-bonding.

Experimental Section

Preparation of Compounds. (a) **Fe(EtEt(dtc))$_2$L,** where L = 1,10-phenanthroline or 2,2′-bipyridine.[25] All operations were performed under an atmosphere of nitrogen. The red-brown air-sensitive compound, Fe(EtEt(dtc))$_2$,[26] (*ca.* 1 g) was suspended in degassed freshly distilled tetrahydrofuran, THF (*ca.* 70 ml). To this was added a THF solution of phen or bipy (equal molar amounts in *ca.* 20 ml of THF). An immediate reaction occurred resulting in deep blue or green solutions from which a crystalline product separated. The compounds were recrystallized from CH_2Cl_2–heptane solution yielding blue (phen) or green (bipy) needles which were dried *in vacuo.*[27] *Anal.* Calcd for (L = phen) $C_{22}H_{28}N_4S_4Fe$: C, 49.61; H, 5.30; N, 10.52. Found: C, 49.90; H, 5.12; N, 10.37. Calcd for (L = bipy) $C_{20}H_{28}N_4S_4Fe$: C, 47.23; H, 5.60; N, 11.02. Found: C, 47.00; H, 5.42; N, 11.23. χ_M^{uncorr} (solid) = 11.57 $\times$ 10^{-3} cgsu/mol for L = phen at 23°. A different synthesis for these compounds was reported by Holah and Murphy[28] during the course of this work.

(b) **Fe(MePh(dtc))$_2$L,** where L = 4,7-dimethyl-1,10-phenanthroline or 4,4′-dimethyl-2,2′-bipyridine. These compounds were prepared in an identical way as in (a). The blue and green needles are air-sensitive and were stored under nitrogen.[27] *Anal.* Calcd for (L = Me$_2$phen) $C_{30}H_{28}N_4S_4Fe$: C, 57.33; H, 4.46; N, 8.91. Found: C, 57.19; H, 4.27; N, 8.67. Calcd for (L = Me$_2$bipy) $C_{28}H_{28}N_4S_4Fe$: C, 55.64; H, 4.64; N, 9.27. Found: C, 55.45; H, 4.67; N, 9.23. χ_M^{uncorr} (solid) = 11.95 and 11.78 $\times$ 10^{-3} cgsu/mol at 23°, respectively, for L = Me$_2$phen and Me$_2$bipy.

(c) **Fe(RR′(dtc))$_3$,** where RR′ = MeBz, MePh, and Me(i-Pr). These compounds were prepared according to the published procedure.[29] They were characterized by elemental analysis, pmr and infrared spectra, and magnetic susceptibility. *Anal.* Calcd for (RR′ = MeBz) $C_{27}H_{30}N_3S_6Fe$: C, 50.29; H, 4.69. Found: C, 50.20; H, 4.69. Calcd for (MePh) $C_{24}H_{24}N_3S_6Fe\cdot0.18CHCl_3$: C, 46.49; H, 3.90; N, 6.74. Found: C, 46.49; H, 3.82; N, 6.79. Calcd for (Me(i-Pr)) $C_{15}H_{30}N_3S_6Fe$: C, 35.96; H, 6.04; N, 8.39. Found: C, 35.81; H, 5.93; N, 8.34. χ_M^{uncorr} (solid) = 10.37, 2.973, and 3.104 $\times$ 10^{-3} cgsu/mol at 23°, respectively.

(d) **[Fe(RR′(dtc))$_3$]BF$_4$,** where RR′ = MeBz, MePh, and Me(i-Pr). These compounds were synthesized according to the procedure of Pasek and Straub.[30] A benzene solution of the appropriate Fe(RR′(dtc))$_3$ complex (b) was saturated with BF_3 for several minutes in a plastic beaker open to the air. The desired salt separated as a black oil which was thoroughly washed with benzene and vacuum dried for several days. The resulting solids were reoiled at least three times from CH_2Cl_2–benzene solution by slow evaporation. They were characterized by elemental analysis, infrared and pmr spectra, and magnetic susceptibility. *Anal.* Calcd for (RR′ = MeBz) $C_{27}H_{30}N_3S_6FeBF_4$: C, 44.33; H, 4.13; N, 5.74. Found: C, 44.54; H, 3.94; N, 5.38. Calcd for (MePh) $C_{24}H_{24}N_3S_6FeBF_4$: C, 41.81; H, 3.51; N, 5.29. Found: C, 41.55; H, 3.96; N, 6.09. Cald for (Me(i-Pr)) $C_{15}H_{30}N_3S_6FeBF_4$: C, 30.67; H, 5.15; N, 7.15. Found: C, 30.81; H, 5.38; N, 6.78. χ_M^{uncorr} (solid) = 3.480, 3.740, and 3.179 $\times$ 10^{-3} cgsu/mol at 23°, respectively.

(e) ***N,N,N′,N′*-Tetramethylthiuram Disulfide, Me$_4$tds.** This compound was prepared according to a literature preparation from MeMe(dtc)Na[31] and was characterized by infrared and pmr spectra and melting point (mp 155–157°, lit.[31] 156°).

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[24] The only quantitative C$\overset{\cdots}{-}$N bond rotation kinetic studies reported to date on transition metal dtc complexes were performed on Fe(dtc)$_2$($S_2C_2Z_2$) complexes where Z is CF_3 or CN. No dependence on Z was found, ref 8 and 9.

[25] Abbreviations used throughout for RR′(dtc) N substituents: methyl = Me, ethyl = Et, isopropyl = i-Pr, benzyl = Bz, phenyl = Ph. Other abbreviations are as follows: 1,10-phenanthroline = phen, bipyridine = bipy.

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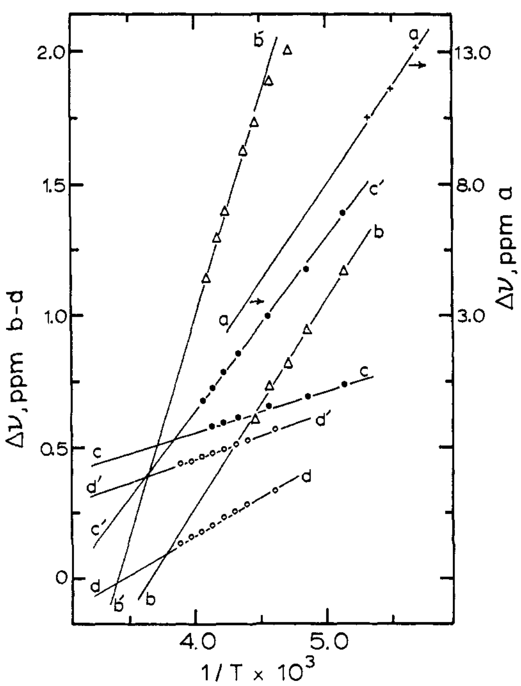

Figure 2. Observed (points) and extrapolated (lines) chemical shift separations *vs.* 1/*T* between exchanging resonances for (a) N-CH$_2$ resonances of Fe(EtEt(dtc))$_2$phen; (b) N-CH$_3$ resonances 1 and 2, (b') 1 and 3 of Fe(Me(*i*-Pr)(dtc))$_3$; (c) N-CH$_3$ resonances 1 and 2, (c') 1 and 3 of [Fe(MeBz(dtc))$_3$]BF$_4$; and (d) N-CH$_3$ resonances 1 and 2, (d') 2 and 3 of [Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$ in CD$_2$Cl$_2$ solution at 100 MHz. Numbers 1, 2, and 3 refer to slow-exchange resonances in order of increasing H.

Pmr Measurements. All spectra were recorded on a Varian XL-100-15 nmr spectrometer equipped with a variable temperature probe. Chemical shifts were measured relative to CHDCl$_2$ solvent resonance by using an electronic counter and the ^{2}H internal lock reference frequency. Kinetic line-shape analyses were performed on spectra recorded well below saturation. Temperatures were measured by a thermocouple mounted in an nmr tube. All spectra were recorded using CD$_2$Cl$_2$ solvent with complex concentrations of *ca.* 0.1 *M*.

Magnetic Measurements. Solid moments were determined by the Faraday method using Hg[Co(SCN)$_4$] as calibrant. Solution moments were determined by the conventional nmr method at 31° using CH$_2$Cl$_2$ solutions *ca.* 5% v/v in TMS. The TMS shifts were used in the calculation. Diamagnetic corrections were calculated from Pascal's constants.

Kinetic Analysis. The iron complexes in this study are of three stereochemical types: M(A-A')$_3$, M(A-A)$_2$B-B, M(A-A')$_2$B-B. The first of these exists as a mixture of cis and trans isomers in solution, and C$\overset{\cdots}{-}$N bond rotation will result in cis–trans isomerization (*vide infra*). The kinetic line-shape analysis involves a three site exchange problem which is shown in Figure 1 for the Me resonances of Fe(Me(*i*-Pr)(dtc))$_3$.[32] Rapid C$\overset{\cdots}{-}$N bond rotation results in random scrambling of these three Me resonances (*vide infra*). Line shapes were simulated by a computer calculation using the Binsch DNMR3 program.[33] A three-site exchange was assumed with $k_{12} = k_{13} = k_{23}$ where k_{ab} is the rate constant for a → b. The best fits to experimental line shapes were visually determined and the resulting values of *k* at various temperatures were taken to be the rate constants for C$\overset{\cdots}{-}$N bond rotation. Linear extrapolations of chemical shift separations, Δν, and line widths at half-height, $H_{1/2}$, from slow-exchange spectra are shown in Figures 2 and 3. Linear extrapolations of Δν *vs.* 1/*T* and ln ($H_{1/2}$) *vs.* 1/*T* plots were used because of approximate linearity in the slow-exchange region and because these extrapolations yielded reasonable $\Delta S^{\ddagger}$ values. This procedure has been used before for paramagnetic complexes.[8,9] Cis and trans populations were nearly statistical (1:3) and ΔF values for cis ⇄ trans were determined from slow-exchange spectra by computer fits. ΔH and ΔS values were determined by least-squares fits to ΔF *vs.* *T* plots and are given in Table II.

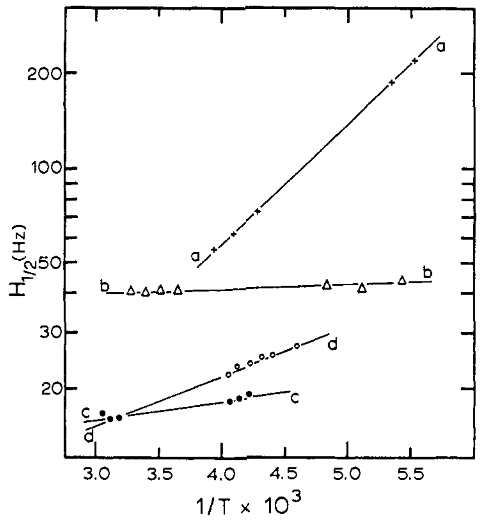

Figure 3. Ln ($H_{1/2}$) *vs.* 1/*T* for (a) N-CH$_2$ resonances of Fe(EtEt(dtc))$_2$phen, (b) N-CH$_3$ resonances of Fe(Me(*i*-Pr)(dtc))$_3$, (c) N-CH$_3$ resonances of [Fe(MeBz(dtc))$_3$]BF$_4$, and (d) N-CH$_3$ resonances of [Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$ in CD$_2$Cl$_2$ solution at 100 MHz.

In complexes of the type M(A-A)$_2$B-B, rapid C$\overset{\cdots}{-}$N bond rotation results in a simple two-site exchange when the A substituent is ethyl. Two equal intensity methylene resonances are observed at low temperatures due to slow C$\overset{\cdots}{-}$N bond rotation (*vide infra*). Rapid C$\overset{\cdots}{-}$N bond rotation will coalesce these lines. No spin–spin coupling was observed because of paramagnetic relaxation.[34] The absence of spin–spin coupling in paramagnetic iron–dtc complexes is common.[8,9,34] Appropriate extrapolations are shown in Figures 2 and 3. A computer simulation of the line shapes was employed based on the Gutowsky–Holm equation for two-site exchange.[35] The rate constants for C$\overset{\cdots}{-}$N bond rotation were determined by visual fits of the calculated to the observed spectra. The rate constant, *k* (sec^{-1}), is defined as $1/\tau$, where τ is the preexchange lifetime of a proton in either environment (τ defined here is equal to 2τ in the Gutowsky–Holm equation). This same procedure was used for the analysis of Me$_4$tds. In this compound the extrapolated slopes and intercepts for Δν (ppm) *vs.* 1/*T* (°K^{-1}) and ln $H_{1/2}$ (ln (Hz)) *vs.* 1/*T* plots are the following: −1.63 ppm °K, 0.0559 ppm; and +217 ln (Hz) °K, −0.959 ln (Hz), respectively.

For complexes of the type Fe(A-A')$_2$B-B, rate constants for C$\overset{\cdots}{-}$N bond rotation were determined by computer fits at one temperature only. Appropriate extrapolations were made for the three-site exchange problem (*vide infra*) as outlined above for Fe(A-A')$_3$ complexes.

Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were determined by least-squares fits to ln (*k*/*T*) *vs.* 1/*T* plots (Figure 4). Errors were estimated from error limits in τ and *T*. Values of $\Delta F^{\ddagger}$ in the region of exchange broadening have considerably smaller error limits (Table III).[3]

Results and Discussion

Magnetic Properties and Stereochemistry of the Complexes. (a) Fe(RR'(dtc))$_2$L Complexes. Fe(EtEt(dtc))$_2$(phen) and -(bipy) have been synthesized by Holah and Murphy.[28] The MePh analogs are new. These complexes which contain iron in a formal oxidation state of II are high-spin d^6 as evidenced by their solid and solution magnetic moments (Table I). They manifest large

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[32] Under conditions of slow cis–trans isomerization, four Me resonances should be observed. Indeed, all four are seen at lower temperatures but above *ca.* −80° these complexes are involved in rapid Λ–Δ optical isomerization *via* a trigonal-twist mechanism. This process coalesces two of the trans Me resonances but does not cause cis–trans isomerization. Thus, three lines result of approximate intensity 2:1:1.[16,17]

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Table I. Magnetic Data for Tris Chelate Dithiocarbamato Complexes in CD_2Cl_2 Solution

Complex	Temp, °C	Pmr shifts, ppm[a]		μ_{eff}, BM Solid (23°)	μ_{eff}, BM CH_2Cl_2 (31°)
$Fe(EtEt(dtc))_2phen$	+31	N-CH_2	−29.78	5.33	*b*
	−91		−78.37, −66.57		
$Fe(EtEt(dtc))_2bipy$	+31	N-CH_2	−30.48	*b*	*b*
	−96		−77.28, −72.10		
$Fe(MePh(dtc))_2Me_2phen$	+11	phen-CH_3	+17.35	5.43	5.21
	−96		−46.50 (1), +33.15 (2), +23.10 (1)[c]		
$Fe(MePh(dtc))_2Me_2bipy$	+31	bipy-CH_3	+11.10	5.40	5.49
	−97		+32.44 (1), +22.74 (2), +13.79 (1)[c]		
$Fe(MeBz(dtc))_3$	+31	N-CH_3	+46.70	5.05	4.06[d]
	−52		C = −32.68; T = −31.42, −31.42		
$Fe(MePh(dtc))_3$	+31	N-CH_3	−38.49	2.81	3.47[d]
	−58		−20.70 (2), 20.08 (1), 19.71 (1)[c]		
Fe(Me(*i*-Pr)(dtc))$_3$	+31	N-CH_3	−45.40	2.82	4.18
	−54		C = −32.04; T = −33.94, −33.20		
$[Fe(MeBz(dtc))_3]BF_4$	+36	N-CH_3	−59.35	3.01	3.02
	−54		C = −92.02; T = −92.66, −91.68		
$[Fe(MePh(dtc))_3]BF_4$	+43	N-CH_3	−57.58	2.95	2.83
	−54		C = −89.34; T = −90.08, −89.87		
[Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$	+43	N-CH_3	−59.60	2.89	2.83
	−56		C = −96.60; T = −97.05, −96.99		

[a] Shifts are relative to $CHDCl_2$ internal standard and were recorded at 100 MHz. C = cis and T = trans, and positive shifts are upfield from $CHDCl_2$. [b] Not enough pure sample for accurate measurement. [c] Numbers in parentheses are the relative intensities. [d] $CHCl_3$ solution: R. E. Eley, R. R. Myers, and N. V. Duffy, *Inorg. Chem.*, **11**, 1128 (1972).

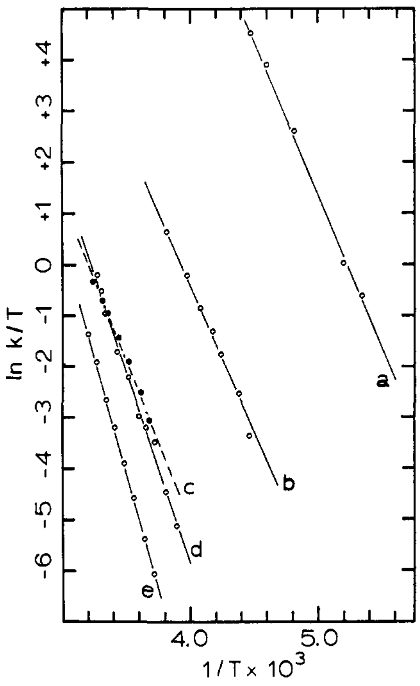
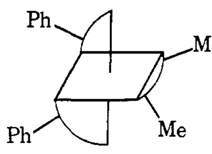


Figure 4. Eyring plots for C$\overset{\cdots}{-}$N bond rotation for (a) Fe(EtEt-(dtc))$_2$phen, (b) Fe(Me(*i*-Pr)(dtc))$_3$, (c) $[Fe(MeBz(dtc))_3]BF_4$, (d) [Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$, and (e) Me_4tds in CD_2Cl_2 solution.

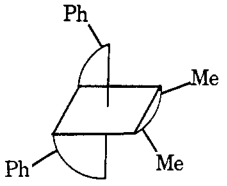
isotropic nmr shifts[36] which have linear $1/T$ temperature dependence. Table I contains the pmr shifts of resonances used in the analysis at two temperatures. The Et_2dtc complexes show one $-CH_3$ and one $-CH_2$ resonance at room temperature. At lower temperatures the $-CH_2$ resonance splits into two peaks of equal intensity while the $-CH_3$ resonance remains unsplit. This observation results from either (i) slow C$\overset{\cdots}{-}$N rotation and fast metal centered inversion, or (ii) slow metal centered inversion and fast C$\overset{\cdots}{-}$N rotation.[8,9] Stereochemically similar complexes, $Fe(EtEt(dtc))_2$-$S_2C_2Z_2$ where Z = CF_3 or CN, have been analyzed and arguments presented in ref 8 and 9 should be referred to.

$Fe(MePh(dtc))_2Me_2phen$ or $-Me_2bipy$ can exist in three geometric isomeric forms (IIa–c) each of which



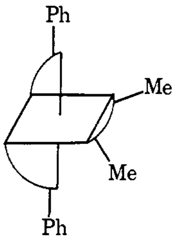
Λ cis,trans

IIa



Λ cis,cis

IIb



Λ trans,cis

IIc

is enantiomeric. Under the conditions of slow C$\overset{\cdots}{-}$N bond rotation the nmr spectrum should consist of four $-CH_3$ resonances from the Me_2phen or Me_2bipy ligand. At room temperature only one $-CH_3$ resonance is observed (Table I). As the temperature is lowered to *ca.* −70° the $-CH_3$ resonance broadens and below *ca.* −95° three distinct peaks grow in with populations *ca.* 2:1:1. This coalescence pattern is identical with the one observed in the ^{19}F spectra of $Fe(MePh(dtc))_2$-$S_2C_2(CF_3)_2$ and has been assigned as resulting from C$\overset{\cdots}{-}$N bond rotation.[8] Only three $-CH_3$ resonances are observed because metal centered inversion is still fast and presumably proceeds by a trigonal-twist

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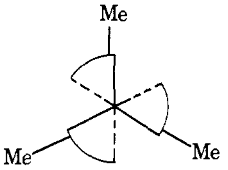
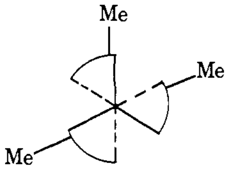
[36] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965); R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

mechanism.[37] The N–CH_3 resonances undergo a similar coalescence in these complexes; however, their broad line width prevents complete resolution. Kinetic parameters for this process are nearly identical with those of Fe(EtEt(dtc))$_2$phen or –bipy (Table III) and therefore this process is tentatively assigned as C$\overset{\cdots}{-}$N bond rotation in these analogs as well (case (i) above).

(b) Fe(RR′(dtc))$_3$ Complexes. These complexes where RR′ = MeBz, MePh, or Me(*i*-Pr) have been reported and their magnetic properties have been thoroughly explored.[38] They have solid and solution magnetic moments (Table I) intermediate between high-spin and low-spin d^5 and have a formal Fe oxidation state of III. They manifest the well-known $^2T_2$–$^6A_1$ spin-state equilibrium.[38] Their pmr shifts show nonlinear $1/T$ temperature dependence, which is consistent with this assignment. In solution these complexes exist in two geometric isomeric forms (IIIa,b) each of which is enantiomeric. If C$\overset{\cdots}{-}$N bond rotation is slow the nmr spectrum should consist of four N–CH_3 resonances. This has been observed below −90° with the MePh complex for which the temperature-dependent spectra have been reported in a preliminary communication.[16] As the temperature is raised two distinct kinetic processes are observed (figure in ref 16). The high-temperature process which consists of three lines coalescing into one (Figure 1) results from cis–trans isomerization and could be caused by C$\overset{\cdots}{-}$N bond rotation.[39] A similar coalescence pattern has been observed in the three Fe(RR′(dtc))$_3$ complexes examined with coalescence occurring between *ca.* −20 and −50°. The low-temperature process is a metal centered rearrangement *via* a trigonal-twist mechanism.[16,17]



Λ cis
IIIa



Λ trans
IIIb

(c) [Fe(RR′(dtc))$_3$]BF$_4$ Complexes. Pasek and Straub[30] reported the synthesis and magnetic and Mössbauer properties of several symmetrically substituted complexes of this type. These compounds are low-spin d^4 and have a formal Fe oxidation state of IV. The complexes examined here are new (RR′ = MeBz, MePh, and Me(*i*-Pr)) and have solid and solution magnetic moments (Table I) which are consistent with this assignment. The variable-temperature pmr shows large isotropic shifts which manifest linear $1/T$ behavior. The temperature-dependent pmr spectra of the MeBz complex have been reported by us in a preliminary communication.[17] The coalescence pattern is identical with that of the corresponding "Fe(III)" complex and therefore amenable to the same assignment. The three peak coalescence (Figure 1 of ref 17) therefore results from cis–trans isomerization and could be caused by C$\overset{\cdots}{-}$N bond rotation. A similar coalescence occurs between 0 and +40° for the three complexes studied. The thermodynamic parameters for cis–trans isomerization are listed in Table II.

Table II. Thermodynamic Parameters for the Cis ⇄ Trans Equilibria of M(RR′(dtc))$_3$ Complexes[a]

Complex	$\Delta H°$, kcal/mol	$\Delta S°$, eu	$\Delta G°_{298}$, kcal/mol	$K_{eq}^{298°}$ = T/C
Fe(Me(*i*-Pr)(dtc))$_3$	+0.72	+5.2	−0.83	4.1
[Fe(MeBz(dtc))$_3$]BF$_4$	−0.15	+1.7	−0.66	3.0
[Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$	+0.17	+2.7	−0.63	2.9

[a] These parameters were determined at three or four temperatures from computer fits to slow-exchange spectra.

All of the above complexes are paramagnetic and therefore manifest large isotropic shifts. These shifts magnify small differences in magnetic environment.[36] The kinetic analyses are simplified by this phenomenon because exchanging environments are usually separated by several ppm and spin–spin coupling is not observed. Line-shape analyses on these broad well-separated resonances are in general more accurate than on similar diamagnetic compounds because small uncertainties in extrapolated frequencies and widths at half-height have little effect on kinetic parameters.

Assignment of C$\overset{\cdots}{-}$N Bond Rotation. In the three classes of compounds discussed above, geometric isomerization could indeed result from rapid C$\overset{\cdots}{-}$N bond rotation. It is also possible that certain metal centered rearrangement reactions could cause the observed isomerization. These reactions have been thoroughly discussed in recent papers.[8,40] The C$\overset{\cdots}{-}$N stretching vibration is intermediate between that normally found for C–N single and C=N double bonds in these complexes (Table III). Indeed, this is a general property of all dtc complexes, esters, and thiuram disulfides. X-Ray crystallographic data also indicate this partial double bond character.[20] Barriers to C$\overset{\cdots}{-}$N bond rotation have been measured for several dtc esters[7] and have been estimated for Co(MeBz(dtc))$_3$.[12] We have measured the barrier in Me$_4$tds in CD_2Cl_2 solution. Table III shows the activation parameters for these compounds in which the kinetic process is unquestionably C$\overset{\cdots}{-}$N bond rotation. The close similarity of these to the activation parameters in the iron complexes provides strong support for the same kinetic process (Table III). Further, the trends in $\Delta F^{\ddagger}$ parallel the trends in ν(C$\overset{\cdots}{-}$N).[41] Fe(EtEt(dtc))$_2$mnt and [Fe(EtEt(dtc))$_3$]BF$_4$ have the highest stretching frequencies (1510 and 1527 cm^{-1}), Fe(EtEt(dtc))$_3$ is lower (1495 cm^{-1}), and Fe(Et$_2$dtc)$_2$phen and –bipy have the lowest (1482 and 1476 cm^{-1}). This same trend is observed with the other R substituents but such a complete comparison is not possible. These trends in

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[37] The trigonal-twist mechanism would indeed average the Me groups of the cis,trans and trans,cis isomers while leaving the two Me's of the cis,cis isomer nonequivalent.[8] This mechanism cannot be definitely assigned here however because complete freezing out of all four peaks is not accomplished. Three resonances have been observed down to −110°.

[38] R. L. Martin and A. H. White, *Transition Metal Chem.*, **4**, 113 (1968), and references cited therein.

[39] In ref 16 we concluded that this high-temperature process was a metal centered rearrangement. This process could equally as well be C$\overset{\cdots}{-}$N bond rotation. Arguments presented below provide strong evidence for the latter assignment.

[40] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970); J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, 10, 1004 (1971); J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 331 (1971); B. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, in press.

[41] The following values were determined for CH_2Cl_2 solutions ~0.1 *M* in complex.

Table III. Kinetic Parameters for C–N Bond Rotation

Compound	$\Delta F^{\ddagger}$(298°), kcal/mol	$\Delta F^{\ddagger}$(°C), kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Solvent	Ref	ν(C–N), cm^{-1}, solution
$Fe(EtEt(dtc))_2phen$	8.80	8.8 ± 1 (−71)	12.3 ± 5	+17 ± 15	CD_2Cl_2	This work	1482
$Fe(EtEt(dtc))_2bipy$	8.2	8.2 ± 1 (−78)	*a*	*a*	CD_2Cl_2	This work	1481
$Fe(MePh(dtc))_2Me_2phen$	8.6	8.5 ± 1 (−77)	*a*	*a*	CD_2Cl_2	This work	*c*
$Fe(MePh(dtc))_2Me_2bipy$	8.5	8.6 ± 1 (−80)	*a*	*a*	CD_2Cl_2	This work	*c*
$Fe(MeBz(dtc))_3$	12.2	12.2 ± 0.3 (−26)	*a*	*a*	CD_2Cl_2	This work	1499
$Fe(MePh(dtc))_3$	12.0	12.0 ± 0.3 (−38)	*a*	*a*	CD_2Cl_2	This work	*c*
Fe(Me(*i*-Pr)(dtc))$_3$	12.0	12.0 ± 0.2 (−33)	12.1 ± 2.0	+1 ± 8	CD_2Cl_2	This work	1481
$[Fe(MeBz(dtc))_3]BF_4$	14.7	14.7 ± 0.2 (25)	13.0 ± 2.0	−5 ± 6	CD_2Cl_2	This work	1535
$[Fe(MePh(dtc))_3]BF_4$	13.6	13.6 ± 0.3 (−6)	*a*	*a*	CD_2Cl_2	This work	1494
[Fe(Me(*i*-Pr)(dtc))$_3$]BF$_4$	14.7	14.7 ± 0.2 (25)	15.1 ± 2.0	+1 ± 5	CD_2Cl_2	This work	1520
$Fe(EtEt(dtc))_2tfd$	15.2	15.2 ± 0.2 (25)	16.4 ± 1.5	+4 ± 5	CD_2Cl_2	8	1507
$Fe(MePh(dtc))_2tfd$	14.9	14.9 ± 0.2 (25)	14.0 ± 2.1	−3 ± 8	CD_2Cl_2	8	1472
$Fe(EtEt(dtc))_2mnt$	14.1	14.1 ± 0.2 (25)	12.5 ± 2.0	−6 ± 6	CD_2Cl_2	9	1510
Me_4tds	15.8	15.8 (25)	17.8	+7 ± 4	CD_2Cl_2	This work[d]	1500
Me_2NCS_2Et	14.6	14.6 (25)	11.5	−10	Hexane	7	1498
Et_2NCS_2Me	15.0	15.0 (25)	11.7	−8	Hexane	7	1489
$Co(MeBz(dtc))_3$	15–20[b]				CD_2Cl_2	12	1500

[a] Computer fit at coalescence temperature only. [b] Estimated from coalescence temperature. [c] Interference from other bands prevents accurate measurement. [d] Activation parameters for Me_4tds have been measured in $CDCl_3$ solution with $\Delta F^{\ddagger}$(301°) = 15.3 kcal/mol: N. K. Wilson, *J. Phys. Chem.*, **75**, 1067 (1971).

ν(C$\overset{\cdots}{-}$N) are meaningful even if the C–N vibration is not a pure one because the comparisons are made with constant N substituent and metal atom. The $\Delta F^{\ddagger}$ (298°) values reflect this order for all the complexes studied. The highest barriers ($\Delta F^{\ddagger}$ = 14–15 kcal/mol) correspond to the high ν(C$\overset{\cdots}{-}$N) values of $Fe(dtc)_2$(dithiolene) and $[Fe(dtc)_3]BF_4$ while the $Fe(dtc)_3$ and $Fe(dtc)_2phen$ –bipy complexes have $\Delta F^{\ddagger}$ of 12.0 and 8.5 kcal/mol, respectively (Table III). These arguments provide good support that rapid C$\overset{\cdots}{-}$N bond rotation causes geometrical isomerization in these complexes.

Ligand exchange cannot account for cis–trans isomerization because experiments on mixed complexes reveal that this process is slow on the pmr time scale at temperatures significantly higher than where cis–trans coalescence occurs. The coalescence pattern for isomerization was simulated assuming random environmental averaging (Experimental Section). Rapid C$\overset{\cdots}{-}$N bond rotation on top of a rapid trigonal-twist metal centered rearrangement predicts this pattern. Figure 1 shows that good agreement was achieved.

Kinetics of C$\overset{\cdots}{-}$N Bond Rotation. Table III contains the kinetic parameters for C$\overset{\cdots}{-}$N bond rotation. Total line-shape analyses were performed on all compounds for which $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are given (see Experimental Section). For the other compounds $\Delta F^{\ddagger}$ was determined near the coalescence point by a computer fit. All of the compounds give $\Delta S^{\ddagger}$ values near zero (±7 eu) with the exception of $Fe(EtEt(dtc))_2phen$. In this case the coalescence point occurred at *ca.* −80° and only several slow-exchange points were available for extrapolation. Therefore, the errors in activation parameters are significantly larger for this compound. The $\Delta F^{\ddagger}(T)$ values in the region of the line broadening are the most accurate parameters. For purposes of comparison the $\Delta F^{\ddagger}$(298°) values were all calculated assuming $\Delta S^{\ddagger} = 0$. This in no way changes any of the trends discussed below and is probably the best way to treat the data.[3]

Examination of the data in Table III reveals three groups of $\Delta F^{\ddagger}$(298°) values. Iron complexes which have a formal oxidation state of IV, *i.e.*, [Fe(RR′(dtc))$_3$]BF$_4$ and Fe(RR′(dtc))$_2$dithiolene,[42] have the highest values (14.1–15.2 kcal/mol). The dtc esters and Me_4tds have barriers in this region also. Significantly lower barriers are found for complexes with a formal oxidation state of III; Fe(RR′(dtc))$_3$ complexes have $\Delta F^{\ddagger}$ (298°) values between 12.0 and 12.2 kcal/mol. The lowest barriers are found for a formal oxidation state of II (8.2–8.8 kcal/mol). These groupings are real and well outside of experimental error. Figure 4 graphically illustrates this result.

This trend may be rationalized by considering resonance structure Ic. High barriers to C$\overset{\cdots}{-}$N bond rotation are expected if this resonance structure is stabilized and *vice versa*. It is well known that this resonance form is important in dtc esters,[7] thiuram disulfides,[11] and dtc complexes.[21] Indeed, this is the reason for their high barriers to C$\overset{\cdots}{-}$N bond rotation and their high values of ν(C$\overset{\cdots}{-}$N) (Table III). The "Fe(IV)" complexes have similar barriers to those of the dtc esters and thiuram disulfides and therefore must possess similar contributions of resonance form Ic. As the formal oxidation state of iron is lowered a sizable decrease in the barrier to bond rotation is observed. Lower ν(C$\overset{\cdots}{-}$N) values are also noted when series with constant nitrogen substituent are compared (*vide supra*). It is obvious that the reduced, more electron rich complexes destabilize Ic. This is best accounted for by increased Fe–S (d_π–d_π) back-bonding. The reduced $Fe(dtc)_2L$ complexes want to get rid of electron density at the metal so they possess the greatest Fe–S back-bonding. These compounds are quickly air oxidized to the corresponding $Fe(dtc)_3$ complexes which is a demonstration of their highly reduced nature. Evidence for d_π–d_π Fe–S bonding in $Fe(dtc)_3$ complexes has recently been published.[43] Indeed, Cotton and McCleverty[44] discussed this bonding mode in mixed dtc–carbonyl complexes of iron. Fe–S back-bonding will

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(42) These complexes are best described as Fe(IV), d^4, complexes because they possess a $S = 0 \rightleftarrows S = 1$ spin-state equilibrium[8-10] and because their Mössbauer spectra are very similar to [Fe(RR′(dtc))$_3$]BF$_4$ complexes: L. H. Pignolet, R. A. Lewis, J. F. Weiher, G. S. Patterson, and R. H. Holm, to be submitted for publication.

(43) R. E. Eley, R. R. Myers, and N. V. Duffy, *Inorg. Chem.*, 11, 1128 (1972).

(44) F. A. Cotton and J. A. McCleverty, *ibid.*, 2, 1398 (1963).

increase electron density on sulfur thereby destabilizing Ic. This would result in a lower barrier to $\mathrm{C}\stackrel{\cdots}{-}\mathrm{N}$ bond rotation. $\mathrm{Fe(dtc)_3}$ complexes must possess less back-bonding and the "Fe(IV)" compounds must have the least. Indeed, the $\Delta F^{\ddagger}$ values of the "Fe(IV)" complexes are nearly identical with the dtc esters and $\mathrm{Me_4}$tds.

The above argument is essentially based on electronic inductive effects. The more oxidized metal will inductively stabilize Ic while the electron rich reduced complex will destabilize this resonance form. Electronic effects of this nature have often been qualitatively observed. Chatt, Duncanson, and Venanzi[21] found that resonance form Ic is important in transition metal dtc complexes and that effects which increase sulfurs ability to accept electrons increase $\nu(\mathrm{C}\stackrel{\cdots}{-}\mathrm{N})$. Cotton and McCleverty[44] showed that $\mathrm{Fe(MeMe(dtc))_2(CO)_2}$ has a much larger $\nu(\mathrm{C}\stackrel{\cdots}{-}\mathrm{N})$ than $\mathrm{Fe(MeMe(dtc))_3}$ because the CO ligand acts as an electron acceptor relative to dtc. Indeed, this is reflected in $\nu(\mathrm{C{\equiv}O})$ which is lowered by *ca.* 15 $\mathrm{cm^{-1}}$ from the analogous $\mathrm{[FeI_2(CO)_2]_n}$ compound. Coucouvanis and Fackler[19] found a direct correlation between the ability of $\mathrm{Ni(dtc)_2}$ compounds to form base adducts and the degree to which Ic is important. This provides good evidence for metal–sulfur π inductive effects.

More striking inductive effects can be seen in the following series of $\mathrm{Sn(MeMe(dtc))_2L_2}$ compounds[23] where LL, $\nu(\mathrm{C}\stackrel{\cdots}{-}\mathrm{N})$ are the following: ClCl, 1546; MeCl, 1536; MeBr, 1524; MeI, 1504; and MeMe, 1490 $\mathrm{cm^{-1}}$. This trend clearly illustrates that as L is more electron withdrawing, the $\mathrm{C}\stackrel{\cdots}{-}\mathrm{N}$ bond order increases. A similar trend was reported by Blaauw, *et al.*,[22] for $\mathrm{(MeMe(dtc))AuL_2}$ complexes where LL, $\nu(\mathrm{C}\stackrel{\cdots}{-}\mathrm{N})$ are the following: MeMe, 1592 and BrBr, 1553 $\mathrm{cm^{-1}}$. These trends clearly show a relation between $\mathrm{C}\stackrel{\cdots}{-}\mathrm{N}$ bond order[45] and electron inductive effects from other ligands.

Barriers to $\mathrm{C}\stackrel{\cdots}{-}\mathrm{N}$ bond rotation should also show an effect of N substituent. The data in Table III show no trends with RR′ for any complex type. Such dependence is presumably within experimental error. It would be expected that the more basic the parent amine the more important Ic will be. However, uniform trends in basicity may be masked by steric effects. A recent publication[43] describes the importance of amine basicity and steric effect for a series of Fe(RR′-(dtc))$_3$ complexes.

Acknowledgments. This research was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the University of Minnesota Graduate School.

[45] Fackler and Coucouvanis showed that a smooth curve relationship exists between bond order and $[\nu(\mathrm{C}\stackrel{\cdots}{-}\mathrm{N})]^2$ for a wide variety of dtc compounds: J.P. Fackler, Jr., and D. Coucouvanis, *Inorg. Chem.*, **7**, 181 (1968).

Mechanisms of the Reactions of Cytochrome *c*. II. The Rate of Reduction of Horse-Heart Ferricytochrome *c* by Chromium(II)[1,2]

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Abstract: The rate of reduction of ferricytochrome *c* by chromium(II) in the presence of various anions has been studied by a flow technique. Measurements in chloride media over the pH range 1–7 revealed a maximum rate at pH ~3.7. Below pH 3, the second-order rate constants (M^{-1} $\mathrm{sec^{-1}}$) are equal to $40/[\mathrm{H^+}]$ while above pH 4.4 the rate constants are given by $3.0 \times 10^3 + 1.0 \times 10^9[\mathrm{H^+}]$ at 25.0° and 1.0 *M* ionic strength. These reactions are interpreted in terms of an electron transfer pathway involving adjacent attack on the iron(III) center. The reduction of ferricytochrome *c* is catalyzed by iodide, azide, and thiocyanate ions. The third-order rate constants (M^{-2} $\mathrm{sec^{-1}}$) for these reactions are the following: iodide, 1.1×10^4 (pH 7.0); azide, 4.1×10^5 (pH 6.1); thiocyanate, 3.7×10^5 (pH 6.1) and 4.7×10^5 (pH 6.5 and 7.0). It is proposed that these reactions feature a remote electron transfer pathway. Similar reactivity patterns ($\mathrm{Cl^-} < \mathrm{I^-} < \mathrm{N_3^-} \sim \mathrm{SCN^-}$) in this and model systems are consistent with this hypothesis.

Cytochrome *c* is a small (molecular weight ~12,400), relatively stable heme protein found in the mitochondria of all aerobic organisms. It is a member of the respiratory chain that affects the oxidation of foodstuffs and the synthesis of adenosine triphosphate. During this process the iron atom of cytochrome *c* is alternately oxidized and reduced; consequently, the electron transfer properties of this protein are intimately related to its function.

Despite extensive studies of oxidation–reduction reactions involving cytochrome *c*,[3–5] the nature of the sites for electron transfer to and from this hemeprotein have

[1] Research performed under the auspices and the U. S. Atomic Energy Commission.

[2] For part I of this series see N. Sutin and J. K. Yandell, *J. Biol. Chem.*, **247**, 6932 (1972).

[3] C. Greenwood and G. Palmer, *ibid.*, **240**, 3660 (1965).

[4] K. G. Brandt, P. C. Parks, G. Czerlinski, and G. P. Hess, *ibid.*, **241**, 4180 (1966).

[5] A. Kowalsky, *ibid.*, **244**, 6619 (1969).