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Kinetic and Mechanistic Study of the Linkage Isomerization of Substituted (5-Phenyltetrazolato)pentaamminecobalt(III) Complexes

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The facile synthesis of a series of (5-(R–phenyl)tetrazolato)pentaamminecobalt(III) complexes which undergo a spontaneous linkage isomerization reaction from the N1- to the N2-bonded linkage isomers is reported for R = 4-CH$_3$, H, 4-Cl, 3-CF$_3$, and 4-NO$_2$. The first-order rate processes show a strong pH dependence with rate constants for the protonated species (k_{3+}) approximately 50 times those of the corresponding deprotonated complexes (k_{2+}). The rate constants and the acid equilibrium constants (K_{a1}) for the N1 complexes show a good correlation with the Hammett σ parameter, while the N2 acid equilibrium constants (K_{a2}, determined separately) correlate well with the σ^- parameter. Kinetic and thermodynamic parameters (k_{3+}, k_{2+}, K_{a1}, and K_{a2}) determined for each system at 25 °C and I = 1.0 M are 3.6×10^{-3}, 4.85×10^{-5}, 0.14, and 0.13; 4.8×10^{-3}, 6.1×10^{-5}, 0.26, and 0.16; 9.4×10^{-3}, 1.40×10^{-4}, 0.40, and 0.27; 2.1×10^{-2}, 2.3×10^{-4}, 1.1, and 0.62; and 3.1×10^{-2}, 5.6×10^{-4}, 1.8, and 2.2 for R = 4-CH$_3$, H, 4-Cl, 3-CF$_3$, and 4-NO$_2$, respectively, where units of s^{-1} for the rate constants and M for the acid dissociation constants are quoted. Relief of steric hindrance as a major driving force for the isomerization is consistent with the data presented. An empirical method for the determination of % N2-bonded species present in N1 preparations is presented.

Introduction

Linkage isomers have fascinated inorganic chemists for many years and have been frequently reviewed.[2] Several pairs have been shown to undergo a spontaneous linkage isomerization reaction, even on such substitutionally inert metals as cobalt(III).[3–9] The majority of studies to date have concentrated on the nitrito–nitro interconversion.[3,10–14] Extensive investigations with various solvents and their kinetic effects are reported in the literature.[14] The novel linkage isomerization of 5-substituted tetrazole complexes reported by Purcell (Scheme I) affords us the opportunity to explore how changes in properties of the isomerizing ligand (e.g., electronic and steric factors) affect the mechanism of interconversion.[15]

To this end a kinetic investigation of the series of pentaamminecobalt(III) complexes utilizing 5-(R–phenyl)tetrazoles as ligands (where R = 4-CH$_3$, H, 4-Cl, 3-CF$_3$, or 4-NO$_2$), and a mechanism consistent with the observed kinetic behavior is proposed.

Experimental Section

All solutions were prepared with in-house distilled water which was passed through a Universal Model I mixed-resin ion-exchange column supplied by Illinois Water Supply Co.

Sodium iodide solutions were made by saturating water with anhydrous NaI (Fisher Scientific Co.) and filtering the resulting solution through a 0.45-μm Millipore filter (Millipore Filter Corp.). Sodium perchlorate solutions were prepared and standardized as described pre-

Scheme I
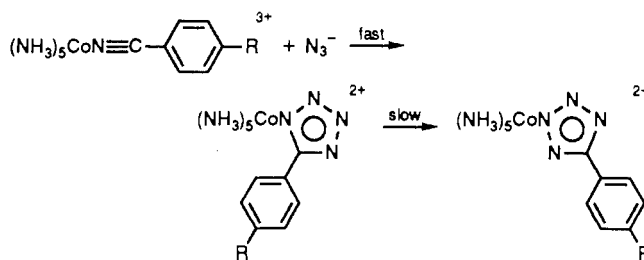
viously.[16] Sodium azide solutions were standardized by using the method of Arnold.[17]

Synthesis. Perchlorate salts of organonitrile complexes were prepared from (trifluoromethanesulfonato)pentaamminecobalt(III) trifluoromethanesulfonate ("triflate") by using the procedure in ref 18. Purity of the organonitrile complexes was established by comparison of visible spectral properties with reported literature values when available (the complex of 3-trifluoromethylbenzonitrile represents the only new nitrile complex in this study).[19–22] Tetrazoles were prepared from their corresponding nitriles (Aldrich Chemical Co., Inc.) by literature methods.[23] Purity was established by comparison of melting points with literature values.[23–27] The 5-(3-(trifluoromethyl)phenyl)tetrazole represents the only new tetrazole in this study. Each tetrazole was converted to its sodium salt for NMR studies by reaction with a stoichiometric amount of NaOH and evaporation to near dryness, followed by filtration.

(3-(Trifluoromethyl)benzonitrile)pentaamminecobalt(III) Perchlorate. The general method of Dixon et al. for weakly coordinating ligands was used.[18] The 3-(trifluoromethyl)benzonitrile was used as received (Aldrich Chemical Co.) without further purification. The complex was recrystallized from water by using HClO$_4$ to induce precipitation. Anal. Calcd for CoC$_8$H$_{19}$N$_6$Cl$_3$F$_3$O$_{12}$: C, 15.66; H, 3.12; N, 13.70. Found: C, 15.58; H, 3.14; N, 13.61. UV–vis λ_{max} (H$_2$O): 467 nm (ϵ = 68.4 M^{-1} cm^{-1}).

5-(3-(Trifluoromethyl)phenyl)tetrazole. The general method of Fin-

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negan et al. was employed.[23] To 8.55 g of 3-(trifluoromethyl)benzonitrile in 25 mL of DMF were added 3.56 g of sodium azide and 2.94 g of ammonium chloride. The slurry was heated with stirring at 100 °C for 2 h and the tetrazole isolated by method A of ref 23. Recrystallization from methanol/water yielded 7.1 g of white solid (66% yield) melting at 152–155 °C.

(5-(3-(Trifluoromethyl)phenyl)tetrazolato-*N1*)pentaamminecobalt(III) Iodide. The compound was prepared from [(NH₃)₅Co(3-CF₃C₆H₄C-N)](ClO₄)₃ as described previously.[8] Precipitating the complex 2 min after sodium azide addition with NaI minimized isomerization to the N2-bonded isomer. Anal. Calcd for CoC₈H₁₉N₉F₃I₂: C, 15.73; H, 3.13; N, 20.63. Found: C, 15.60; H, 3.20; N, 20.48. UV–vis λ_{max} (H₂O): 474 nm (ϵ = 66 M⁻¹ cm⁻¹).

(5-(4-Methylphenyl)tetrazolato-*N2*)pentaamminecobalt(III) Perchlorate. This complex was prepared from [(NH₃)₅Co(4-CH₃C₆H₄C-N)](ClO₄)₃ as described previously.[8] Precipitating the complex 1 h after sodium azide addition with NaClO₄ minimized isomerization to the N2-bonded isomer. The complex analyzed as a mixture of 2+ and 3+ salts, hence leading to fractional atom counts. Anal. Calcd for CoC₈H₂₂.₃₅N₉Cl₂.₃₅O₉.₃₅: C, 17.88; H, 4.19; N, 23.46. Found: C, 17.92; H, 4.12; N, 23.38. UV–vis λ_{max} (H₂O): 464 nm (ϵ = 72.6 M⁻¹ cm⁻¹), 244 nm (ϵ = 23 420 M⁻¹ cm⁻¹).

(5-(4-Chlorophenyl)tetrazolato-*N2*)pentaamminecobalt(III) Iodide. Complete conversion of N1-bonded [(NH₃)₅Co(4-ClC₆H₄CN₄)]I₂ to the N2-bonded form is accomplished by dissolving the N1-bonded complex in a minimum of H₂O and allowing the solution to sit in excess of 5 h, at which time the complex is precipitated with saturated sodium iodide solution and recrystallized from H₂O with sodium iodide. The visible spectrum was obtained from the iodide salt of the complex while the ultraviolet spectrum utilized the perchlorate salt obtained as described below. Anal. Calcd for CoC₇H₁₉N₉I₂Cl: C, 14.56; H, 3.32; N, 21.83. Found: C, 14.37; H, 3.38; N, 21.56. UV–vis λ_{max} (H₂O): 464 nm (ϵ = 68.5 M⁻¹ cm⁻¹); λ_{max} (H₂O): 246 nm (ϵ = 21 780 M⁻¹ cm⁻¹).

(5-(3-(Trifluoromethyl)phenyl)tetrazolato-*N2*)pentaamminecobalt(III) Iodide. Complete conversion of N1-bonded [(NH₃)₅Co(3-CF₃C₆H₄C-N₄)]I₂ to the N2-bonded form is accomplished by dissolving the N1-bonded complex in a minimum of H₂O and allowing the solution to sit in excess of 2 h, followed by a normal precipitation and recrystallization as described above. The visible spectrum was obtained from the iodide salt of the complex while the ultraviolet spectrum utilized the perchlorate salt obtained as described below. Anal. Calcd for CoC₈H₁₉N₉F₃I₂·2H₂O: C, 14.85; H, 3.58; N, 19.48. Found: C, 15.85; H, 3.26; N, 19.39. UV–vis λ_{max} (H₂O): 463 nm (ϵ = 72.3 M⁻¹ cm⁻¹), 239 nm (ϵ = 19 800 M⁻¹ cm⁻¹).

Conversion of Iodide Salts to Perchlorate Salts. Approximately 1 g of the iodide salt of a complex was dissolved in a minimum of H₂O and passed through an anion-exchange column (Dowex 1-X8-100) that had previously been converted to the perchlorate form with sodium perchlorate. The solution of the perchlorate salt was then frozen by using a dry ice/acetone bath and placed in a freeze-dryer (Virtis manifold freeze-dryer, Model 10-131). After all ice external to the freeze-dryer had melted (implying >98% water removal) the sample was washed with 95% ethanol, followed by ether, and air-dried on a fritted filter. The samples were stored under vacuum until the remaining moisture had been removed. Samples of N1-bonded complexes showed no evidence of significant isomerization provided that the amount of preparatory time spent on the ion-exchange column was minimized (<5 min).

Physical Measurements. Ultraviolet and visible spectra were recorded on a Cary 17 spectrophotometer. All spectral information reported for the UV spectra involved perchlorate salts of the respective complexes. The infrared spectra, on samples as KBr pellets, were recorded on a Perkin-Elmer 599 spectrophotometer. A Radiometer Model 26 pH meter equipped with a glass combination electrode (calomel reference) was used to obtain all pH measurements. Since many complexes were in the perchlorate form, NaCl was substituted for KCl in the electrode. Calibration was achieved with Fisher certified standard buffers at two pH values. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Routine proton NMR spectra were obtained on a Hitachi Perkin Elmer R-600 60-MHz FT NMR instrument. Successive ¹H and ¹⁹F NMR spectra of isomerizing systems were obtained in D₂O solutions on a Varian VXR-400 multinuclear NMR instrument. Single 90° pulses (42.5 μs for ¹H, 42 μs for ¹⁹F) were taken at various times during the isomerization process (see Discussion). The sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid, DSS (Aldrich Chemical Co., Inc.), was the internal ¹H shift reference while the trifluoromethanesulfonate anion of the complexes was employed as the ¹⁹F shift reference.

Acid Dissociation Constants. All spectrophotometric K_a measurements were determined at 25 °C in the near-ultraviolet region of the spectrum. Absorbance measurements (A_{obs}) were made for four to eight solutions of varying hydrogen ion concentration (HClO₄), and the ionic strength

was maintained at 1.00 M (NaClO₄). The absorbance values for the deprotonated forms of the complexes were determined in pH 5–7 acetate buffer solutions. The cobalt complex concentrations were approximately 10⁻⁴ M for each spectral determination. The acid dissociation constant of the N2 complexes, K_{a2}, was evaluated from the slopes of plots of (ϵ_{obs} – ϵ_{2+})/[H⁺] vs ϵ_{obs} (K_{a2} = –1/slope).[15]

Kinetic Measurements. The kinetics of the linkage isomerization of the 5-(R-phenyl)tetrazole complexes were studied at wavelengths of 242, 240, 245, and 296 nm for the R = 4-CH₃, H, 4-Cl, and 4-NO₂ ligands, respectively. 5-(3-Trifluoromethylphenyl)tetrazole was studied at λ = 240 nm and λ = 249 nm, and good agreement was found at both wavelengths. These wavelengths all correspond to the appearance of product.

All kinetic measurements were recorded on a Cary 17 spectrophotometer. The temperature was held constant by using a Forma Scientific Model 2095 refrigerated and heated water bath and circulator. Temperature variation during kinetic measurements was held to less than a tenth of a degree. At least two (and usually more) kinetic runs were performed for each solution at each temperature. The reactions were performed at unit ionic strength (maintained with standard NaClO₄ solution). The pH was adjusted by using standardized perchloric acid. Rate constants were obtained from a plot of ln (A_t – A_∞) vs time (k = –slope), where A_t and A_∞ are the absorbances at time t and after the reaction was complete, respectively. All plots for the kinetic runs were linear (R > 0.99) for over 5 half-lives (greater than 90% of the reaction). Each complex was studied at three different temperatures (15, 25 and 35 °C for (5-(4-nitrophenyl)tetrazolato)pentaamminecobalt(III) and 25, 35 and 40 °C for all others). Ten different hydrogen ion concentrations were investigated at each temperature. The concentrations of complex employed in this study ranged between 5 × 10⁻⁴ and 1 × 10⁻⁵ M. The concentration of acid was always greater than 10 times that of the complex to ensure pseudo-first-order behavior. The rate constant of the deprotonated complex, k_{2+}, was evaluated directly from measurements of k_{obs} in 1 M acetate buffers at high pH (5–7). Best-fit values of the rate constant for the protonated species, k_{3+}, and K_{a1} (see eq 4) were obtained from a Marquardt nonlinear least-squares package provided by Statistical Analysis System using an IBM 4381-P2 system operating on release MVS/SP1 of the MVS/JES2 operating system.

Activation parameters were calculated for the rate constants k_{2+} and k_{3+} by plotting ln (k/T) vs 1/T where $\Delta H^\ddagger$ = –(slope × R) and $\Delta S^\ddagger$ = [intercept – ln (k_b/h)]R. Enthalpies and entropies for the acid equilibrium constant, K_{a1}, were obtained from plots of ln K_a vs 1/T giving ΔH_a = –(slope × R) and ΔS_a = (intercept × R).

Determination of Percent N2-Bonded Impurity. Approximately 8 mg of (5-(4-nitrophenyl)tetrazolato)pentaamminecobalt(III) perchlorate was dissolved in 5 mL of H₂O. Spectral scans using an expanded scale (3 nm/in. and 2 s/nm) were recorded at 25 °C as a function of time in the UV region (350–210 nm) until the reaction had reached completion. The rate constant, k, was calculated at two wavelengths (λ = 296 and 299 nm), and an average value was utilized in the remaining calculations. The absorbance at t = 0 s, A_0, was then calculated from eq 1, where A_∞ is the absorbance at t = ∞ and A_t is the absorbance at any time t.

$$A_0 = A_\infty - \{(A_\infty - A_t)e^{kt}\} \qquad (1)$$

The percentage of N2-bonded isomer was then empirically established by plotting A_0 vs A_∞ at 3-nm intervals in groups of six points, until a straight line, which had an intercept of approximately zero, was obtained, implying a region where the N1-bonded complex did not absorb significantly. For the 5-(4-nitrophenyl)tetrazole example, these conditions were met at λ = 320–335 nm. The percent N2 impurity is given by the slope of this line.

The absorbance due to the N2-bonded isomer in the original (t = 0) scan was calculated from eq 2 and the N1 absorbance was calculated from eq 3, where C_T is the total concentration of complex.

$$A_2 = A_\infty([N2]/C_T) \qquad (2)$$

$$A_1 = A_0 - A_2 \qquad (3)$$

Results

Each complex was studied over a 30 °C range and 10 different hydrogen ion concentrations. The rate constants obtained are consistent with the following rate law:

$$\text{rate} = k_{obs}[\text{complex}] = \frac{k_{3+} + k_{2+}K_{a1}[H+]^{-1}}{1 + K_{a1}[H^+]^{-1}} \qquad (4)$$

Plotting k_{obs} vs pH gives a S-shaped titration curve with linear regions asymptotically approaching k_{2+} and k_{3+} at the high and low pH limits of this study, respectively. The midpoint of the

Table I. Kinetic Parameters for Complexes of 5-R-Tetrazoles as a Function of Temperature at I = 1.0 M (NaClO₄)

R	temp, °C	k_{2+}, s⁻¹	k_{3+}, s⁻¹	K_{a1}, M
4-C₆H₄CH₃	25	(4.90 ± 0.15) × 10⁻⁵	(3.66 ± 0.04) × 10⁻³	0.146 ± 0.01
	35	(2.06 ± 0.06) × 10⁻⁴	(1.25 ± 0.01) × 10⁻²	0.159 ± 0.01
	45	(8.42 ± 0.25) × 10⁻⁴	(4.38 ± 0.11) × 10⁻²	0.197 ± 0.02
C₆H₅	25	(6.59 ± 0.20) × 10⁻⁵	(4.83 ± 0.10) × 10⁻³	0.265 ± 0.02
	35	(2.13 ± 0.07) × 10⁻⁴	(1.57 ± 0.01) × 10⁻³	0.241 ± 0.01
	45	(1.03 ± 0.03) × 10⁻³	(5.21 ± 0.10) × 10⁻²	0.274 ± 0.01
4-C₆H₄Cl	25	(1.36 ± 0.04) × 10⁻⁴	(9.89 ± 0.45) × 10⁻³	0.411 ± 0.05
	35	(5.80 ± 0.17) × 10⁻⁴	(2.68 ± 0.07) × 10⁻²	0.390 ± 0.02
	45	(1.90 ± 0.06) × 10⁻³	(9.49 ± 0.44) × 10⁻²	0.421 ± 0.04
3-C₆H₄CF₃	25	(2.21 ± 0.07) × 10⁻⁴	(2.03 ± 0.10) × 10⁻²	1.07 ± 0.20
	35	(9.76 ± 0.29) × 10⁻⁴	(6.63 ± 0.31) × 10⁻²	1.10 ± 0.23
	45	(3.23 ± 0.10) × 10⁻³	(1.79 ± 0.13) × 10⁻¹	1.00 ± 0.18
4-C₆H₄NO₂	15	(1.27 ± 0.04) × 10⁻⁴	(8.16 ± 0.56) × 10⁻³	1.78 ± 0.18
	25	(6.06 ± 0.20) × 10⁻⁴	(3.90 ± 0.17) × 10⁻²	1.84 ± 0.25
	35	(2.09 ± 0.06) × 10⁻³	(1.09 ± 0.11) × 10⁻¹	1.98 ± 0.27

Table II. Rate Constants at 25 °C and I = 1.0 M (NaClO₄) and Activation Parameters for Deprotonated Tetrazole Complexes

5-substituent	k_{2+}, s⁻¹	$\Delta H^{\ddagger}$, kcal mol⁻¹	$\Delta S^{\ddagger}$, cal deg⁻¹ mol⁻¹
4-C₆H₄CH₃	(4.85 ± 0.15) × 10⁻⁵	26.2 ± 0.3	9.5 ± 1.1
C₆H₅	(6.09 ± 0.18) × 10⁻⁵	25.2 ± 2.7	6.9 ± 8.7
4-C₆H₄Cl	(1.40 ± 0.04) × 10⁻⁴	24.3 ± 1.0	3.9 ± 1.7
3-C₆H₄CF₃	(2.28 ± 0.07) × 10⁻⁴	24.7 ± 1.1	7.6 ± 3.6
4-C₆H₄NO₂	(5.61 ± 0.17) × 10⁻⁴	24.1 ± 1.2	7.6 ± 4.0

Table III. Rate Constants at 25 °C and I = 1.0 M (NaClO₄) and Activation Parameters for Protonated Tetrazole Complexes

5-substituent	k_{3+}, s⁻¹	$\Delta H^{\ddagger}$, kcal mol⁻¹	$\Delta S^{\ddagger}$, cal deg⁻¹ mol⁻¹
4-C₆H₄CH₃	(3.60 ± 0.18) × 10⁻³	22.8 ± 0.6	6.7 ± 1.9
C₆H₅	(4.76 ± 0.24) × 10⁻³	21.8 ± 0.5	3.9 ± 1.7
4-C₆H₄Cl	(9.36 ± 0.47) × 10⁻³	20.7 ± 1.8	1.5 ± 6.0
3-C₆H₄CF₃	(2.07 ± 0.10) × 10⁻²	19.9 ± 0.7	0.6 ± 2.1
4-C₆H₄NO₂	(3.08 ± 0.15) × 10⁻²	22.2 ± 0.3	9.2 ± 1.2

titration curve is the K_{a1} of the N1-bonded complex. Table I lists these values as a function of temperature. In general, the rate constant of the protonated tetrazoles, k_{3+}, was approximately 50 times that of the deprotonated complexes, k_{2+}. A 10 °C increase in temperature generally resulted in a tripling of the observed rate constant, k_{obs}.

The entropies and enthalpies of activation were calculated from standard Eyring plots. The activation parameters along with the kinetic data extrapolated to 25 °C are listed in Tables II–IV.

The Eyring plots of k_{2+} for the five complexes studied all have roughly parallel slopes, implying near constant enthalpies of activation, $\Delta H^{\ddagger}$. The same holds true within the k_{3+} series although the values differ between the two series. Comparing $\Delta H^{\ddagger}$ values listed in Tables II and III shows a constant difference of approximately 3 kcal/mol between the k_{2+} and k_{3+} enthalpies of activation, which is approximately the strength of a hydrogen bond to a nitrogen atom. The ΔH_a values for the acid dissociation constant, K_{a1}, for the five N1-bonded complexes studied, showed little or no temperature dependence over the 30 °C temperature range. The kinetic parameters all gave a good (R = 0.98–0.99)

Table IV. Acid Dissociation Constants at 25 °C and I = 1.0 M (NaClO₄) and Thermodynamic Parameters for Tetrazole Complexes

5-substituent	K_{a1}, M	ΔH_a, kcal mol⁻¹	ΔS_a, cal deg⁻¹ mol⁻¹
4-C₆H₄CH₃	0.143 ± 0.007	2.8 ± 0.8	5.6 ± 2.5
C₆H₅	0.256 ± 0.013	0.3 ± 1.2	-1.7 ± 4.0
4-C₆H₄Cl	0.402 ± 0.020	0.2 ± 0.7	-1.1 ± 2.3
3-C₆H₄CF₃	1.09 ± 0.05	-0.7 ± 0.7	-1.9 ± 2.2
4-C₆H₄NO₂	1.81 ± 0.09	0.9 ± 0.2	-4.4 ± 0.7

Table V. Linear Free Energy Relationship Best-Fit Parameters

variable	ρ	R
k_{2+}[a]	1.16 ± 0.06	0.996
k_{3+}[a]	1.06 ± 0.12	0.981
K_{a1}[a]	1.21 ± 0.12	0.985
K_{a2}[b]	0.87 ± 0.09	0.986

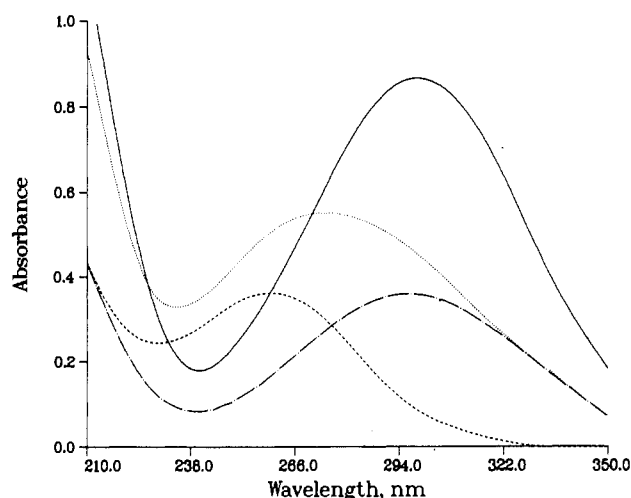[a] Plotted versus σ. [b] Plotted versus σ^-.

Figure 1. Absorbance versus wavelength traces used in determination of percent N2-bonded impurity in an N1-bonded sample (see text) of the (4-nitrophenyl)tetrazolato complex of pentaamminecobalt(III). Legend: (- -) absorbance at t = 0; (—) absorbance at t = ∞; (- - -) absorbance contribution of N1 at t = 0; (-·-) absorbance contribution of N2 at t = 0.

fit in linear free energy diagrams (LFER) when plotted vs Hammett σ values. A good correlation with the Hammett σ^- seems unlikely although only one point would be expected to deviate (that due to 5-(4-nitrophenyl)tetrazole).

Spectrophotometric Acid Dissociation Constants. A spectroscopic determination of the acid dissociation constant for the series of N2-bonded complexes[15] showed a large dependence on the relative electron-withdrawing ability of the phenyl group substituent. Values obtained for K_{a2} at 25 °C and I = 1.0 M (HClO₄/NaClO₄) are 0.13 ± 0.02 M, 0.16 ± 0.01 M, 0.27 ± 0.01 M, 0.62 ± 0.09 M, and 2.20 ± 0.25 M for R = 4-CH₃, H, 4-Cl, 3-CF₃, and 4-NO₂ respectively. Two major differences between the K_a values of the N1- and N2-bonded isomers are the generally lower acidities of the N2-bonded complexes and the good correlation (R = 0.98) with the Hammett σ^- parameter found for the N2 acid dissociation constants (versus σ for K_{a1}). Table V lists ρ and R for the four LFER's in this study.

Determination of Percent N2-Bonded Impurity. The method described here was successfully used on a sample of each of the five complexes in this study. Since the results of the method are meaningful only for the particular sample of interest, only one case, that of the 5-(4-nitrophenyl)tetrazole complex will be presented here. Figure 1 shows the resulting absorbance scans as a function of wavelength for the sample described below. The absorbance at t = 0, A_0, is the sum of the contributions of the absorbances of the N1 (A_1) and N2 (A_2) isomers present in solution at that time. At t = ∞, all the N1 isomer present in solution is converted to N2, resulting in the $A_∞$ plot.

The sample of (5-(4-nitrophenyl)tetrazolato)pentaammine-cobalt(III) perchlorate used in this study was found to contain 41% N2-bonded complex. The least-squares plot of A_0 vs A_∞ had a slope = 0.415 ± 0.005, intercept = 0.013 ± 0.002, and correlation coefficient, R, = 0.9997. The λ_{max} for the N1-bonded isomer was 263 nm with a slightly reduced molar absorptivity (ϵ = 11 150 M^{-1} cm^{-1}) than that found for the N2-bonded isomer, λ_{max} = 296 nm (ϵ = 15 800 M^{-1} cm^{-1}). From the plot of absorbance versus wavelength in Figure 1, we see that the N1-bonded isomer is clearly not absorbing significantly at the wavelengths (λ = 335–320 nm) used to obtain the percent N2-bonded isomer.

Discussion

Although several studies of linkage isomerization reactions have been reported in the literature,[2–14] the ligands' compositions did not permit separation of steric and electronic effects. With the synthesis of the 5-(R–phenyl)tetrazole complexes reported in this study, the establishment of linear free energy relationships (LFER) between the kinetic parameters and Hammett's σ or σ^-, under constant steric conditions, provides a new tool in the understanding of ligand–metal interactions. The reaction times chosen as optimum for the isolation of N1-bonded tetrazoles corresponds to approximately 6–10 half-lives for the attack of 1 M azide in pH 5–6 acetate buffer ensuring <1% nitrile remaining. For the 3-(trifluoromethyl)benzonitrile complex, no previous determination of the rate of azide attack had been established. An estimate was obtained by using the Hammett relation established by Purcell et al.[21]

The pH was controlled with acetate buffer to prevent the attack of the hydroxide anion, which occurs at a much faster relative rate than azide attack.[28] Fortuitously, the rate of isomerization of the N1 species, once formed, is considerably slower than that found for azide attack at this pH. This, coupled with the use of low temperatures (5–15 °C) for recrystallizations and rapid manipulations if and when anion exchange was employed (see Experimental Section), allowed the isolation of N1 complexes, often with less than 10% N2-bonded impurity.

The five complexes chosen provide a group with members equally spaced over a wide range of electron-donating capacity as measured by using the Hammett σ parameter. The 5-substituents in decreasing order of their relative electron-withdrawing abilities are $4\text{-}NO_2C_6H_4$, $3\text{-}CF_3C_6H_4$, $4\text{-}ClC_6H_4$, C_6H_5, and $4\text{-}CH_3C_6H_4$. As free ligands, tetrazoles behave as weak acids, similar to carboxylic acids in strength. In each case, the ligand became more acidic by approximately 4 pK_a units upon coordination to the metal. This effect was previously noted in both 5-methyltetrazole[8] and the isoelectronic 4-methylimidazole[9] when coordinated to a pentaamminecobalt(III) moiety. The N1-bonded complexes were generally found to be slightly more acidic than the corresponding N2-bonded isomers. The measurement of the acid dissociation constants of the N1- and N2-bonded isomers, K_{a1} and K_{a2}, respectively, utilized two different techniques. The K_{a1} values resulted from a kinetic study as a function of pH, while the K_{a2} values were obtained from a direct spectroscopic technique.

Previous studies have shown that no detectable ligand dissociation occurs during the N1-to-N2 linkage isomerization of the pentaamminecobalt(III) complexes of both 5-methyltetrazole and 5-phenyltetrazole.[8] It has also been demonstrated that the isomerization of the 5-methyltetrazolato complex proceeds essentially (98 ± 3%) to completion.[15] However, this latter fact has not been established for the new 5-(R–phenyl)tetrazolato complexes of this study. Figure 2 shows the ¹H NMR spectra in D₂O of the 5-(4-methylphenyl)tetrazolato complex in the methyl region at various times during the isomerization process. In order to minimize the amount of N2-bonded complex (CH₃ resonance at 2.43 ppm vs DSS) present at the start of this series of spectra, the complex was precipitated 45 min after the addition of sodium azide to the nitrile complex rather than the 1 h specified in the Experimental Section. This lead to the presence of 12% (4-
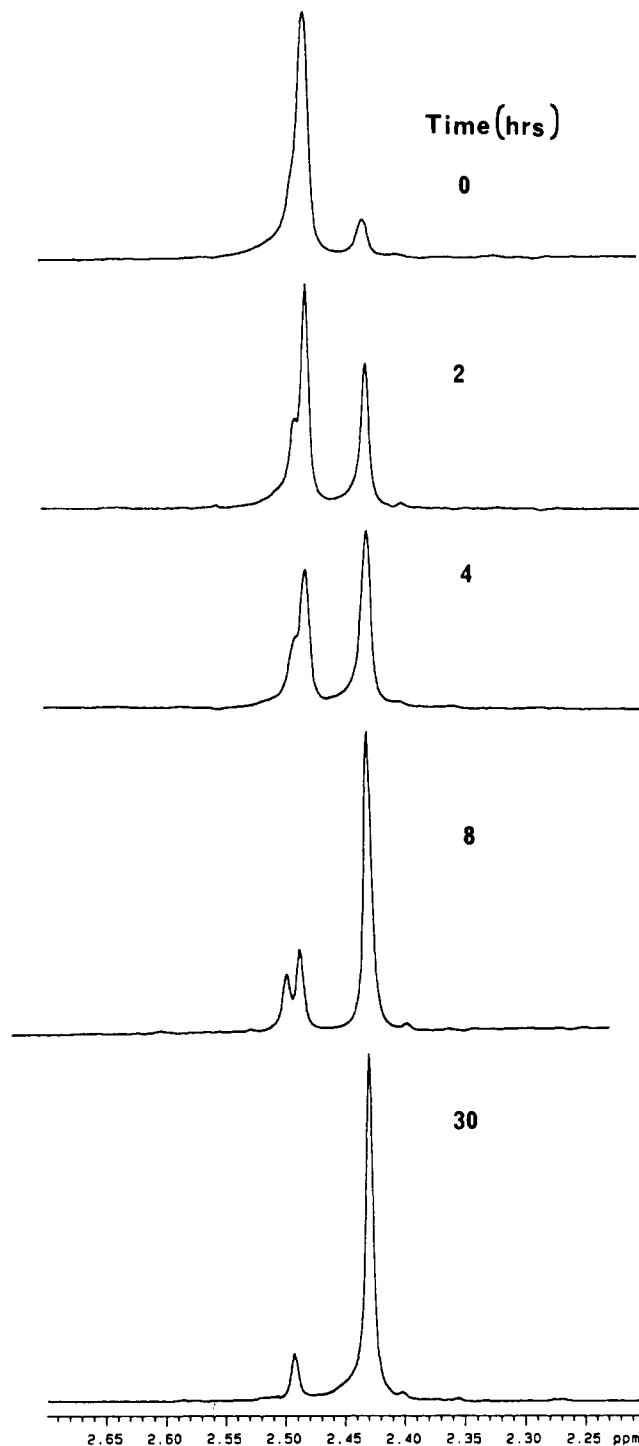
(28) Lopez de la Vega, R.; Ellis, W. R.; Purcell, W. L. *Inorg. Chim. Acta* **1983**, *68*, 97.

Figure 2. ¹H NMR spectra of CH₃ protons for the (5-(4-methylphenyl)tetrazolato)pentaamminecobalt(III) complex in D₂O. Chemical shifts are given versus DSS.

methylbenzonitrile)pentaamminecobalt(III) in the sample (CH₃ resonance at 2.49 ppm vs DSS). As can be seen from Figure 2, no detectable signal from the N1-bonded complex (2.48 ppm) remains after 30 h (~7 half-lives) at 27 °C. Also, since the CH₃ resonance of the sodium salt of 5-(4-methylphenyl)tetrazolate(−1), determined in a separate experiment, occurs at 2.35 ppm vs DSS in D₂O, Figure 2 verifies the lack of any significant ligand dissociation during the isomerization process.

Figure 3 presents a similar series of NMR spectra for the ¹⁹F signal of the CF₃ group of the 5-(3-(trifluoromethyl)phenyl)-tetrazolato complex of pentaamminecobalt(III). Chemical shifts of these D₂O solutions are relative to the ¹⁹F signal of trifluoromethanesulfonate, which was the counteranion of the complex in these studies. Figure 3 also shows that the isomerization proceeds with essentially complete conversion of the N1-bonded
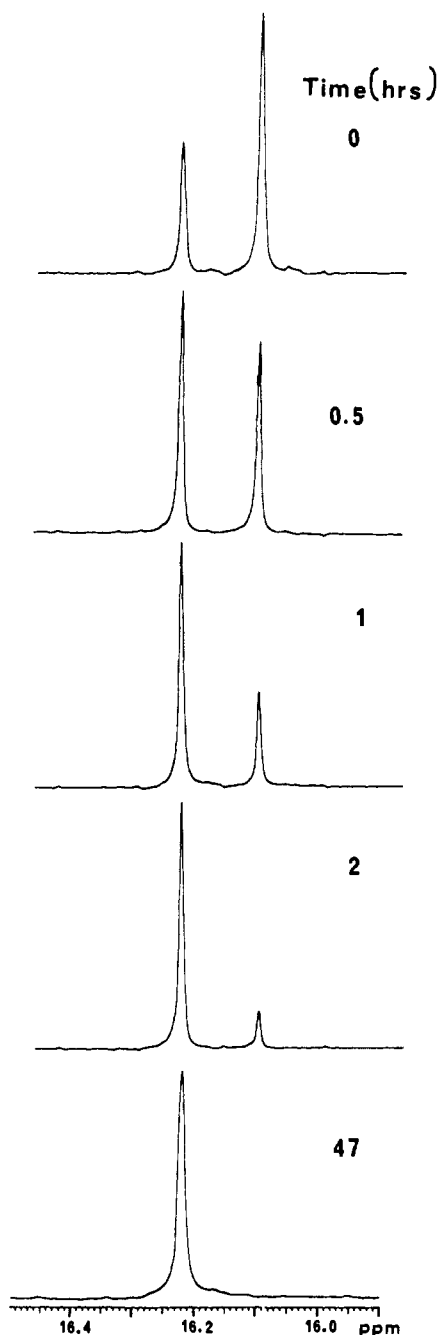
Figure 3. ^{19}F NMR spectra of CF_3 fluorines for the (5-(3-trifluoro-methylphenyl)tetrazolato)pentaamminecobalt(III) complex in D_2O. Chemical shifts versus trifluoromethanesulfonate (1-).

isomer (CF_3 resonance at 16.1 ppm) to the N2-bonded form (CF_3 resonance at 16.2 ppm) after 47 h ($\sim$50 half-lives) at 27 °C. Also, as with the 4-methylphenyl system discussed above and the 5-methyltetrazole and 5-phenyltetrazole systems reported previously,[8] no significant ligand dissociation has occurred. This is apparent from Figure 3 due to the absence of a signal at 16.0 ppm, the position of the CF_3 resonance of the 5-(3-(trifluoromethyl)-phenyl)tetrazolate anion (vs sodium triflate, determined in a separate experiment in D_2O).

A large dependence of the rate of linkage isomerization on the hydrogen ion concentration was found similar to that described by Purcell for the complex of 5-methyltetrazole.[15] This requires competitive reactions in which the protonated and deprotonated forms isomerize at different rates, with rate constants k_{3+} and k_{2+}, respectively, as shown in Scheme II. In all cases studied, the rate of isomerization of the protonated species was approximately 50 times faster than that of the deprotonated species. The rate expression for this reaction is shown in eq 4. Determination of the rate constants k_{2+} and k_{3+} is facilitated by the limiting cases
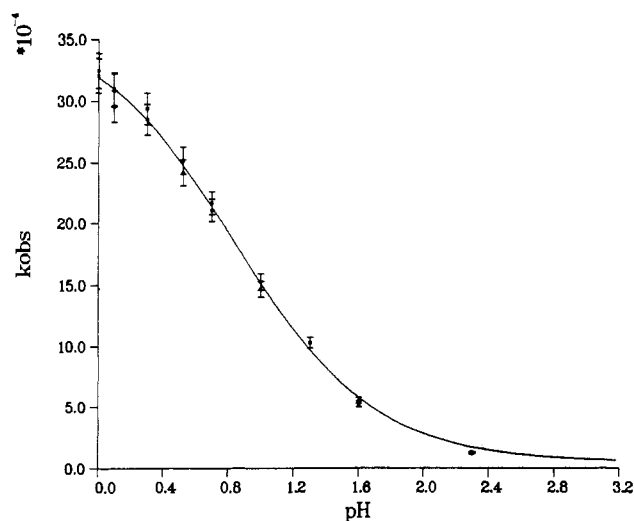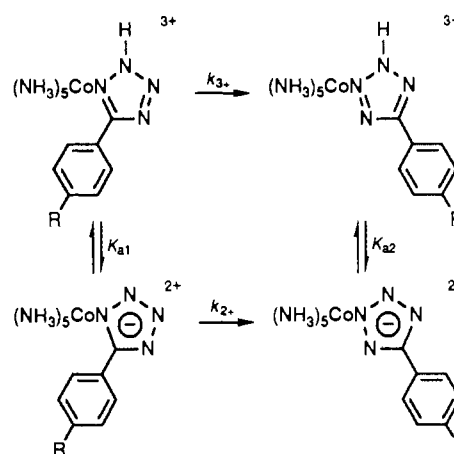
Scheme II

Figure 4. Rate constant versus pH for the (4-methylphenyl)tetrazolato complex linkage isomerization at 25 °C and $I = 1.0$ M.
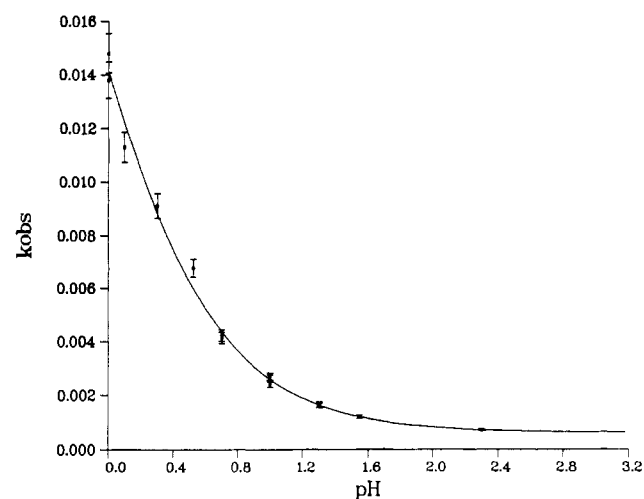

Figure 5. Rate constant versus pH for the (4-nitrophenyl)tetrazolato complex linkage isomerization at 25 °C and $I = 1.0$ M.

found at high and low pH. As the pH increases, k_{obs} approaches k_{2+} asymptotically. Conversely, as the pH decreases, k_{obs} approaches k_{3+} in the limit. Unfortunately, since the ionic strength is required to be one, a pH of zero is the lower limit. Consequently, for the 5-(4-methylphenyl)tetrazole at 25 °C, with a K_{a1} of 0.146 M, k_{obs} at pH = 0 was approximately 89% of the actual k_{3+} (Figure 4), while for 5-(4-nitrophenyl)tetrazole with a K_{a1} of 1.8 M, k_{obs} at pH = 0 is only 34% of the calculated k_{3+} (Figure 5).

The 5-(4-nitrophenyl)tetrazole system is unique among the five systems studied in that a conjugated pathway exists between the

Table VI. Linkage Isomerization Kinetic Parameters for Pentaamminecobalt(III) Complexes

ligand	k at 60 °C, s^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
4-methylimidazole[a]	$(5.8 \pm 2.2) \times 10^{-8}$		
4-methylimidazolato[a]	3.5×10^{-5}	32.4 ± 4.1	16.7 ± 11.7
5-methyltetrazole[b]	5.6×10^{-3}	15 ± 4	-24 ± 13
5-methyltetrazolato[b]	2.1×10^{-4}	26.0 ± 1.8	2.5 ± 5.6
nitrito[c]	5.3×10^{-3}	22.7 ± 1	-1.0 ± 2.9

[a] Reference 9. [b] Reference 15. [c] Reference 10.

nitro group and the tetrazole moiety. Model studies show that in the N1-bonded isomer the phenyl ring and the tetrazole ring are forced out of their coplanar configuration, and therefore, the conjugated pathway can no longer exist. Because of this steric hindrance, one would expect the K_a's of the N1-bonded isomers utilized in this study to correlate with the Hammett σ parameter, which does not include through resonance effects. The K_a's of the N2-bonded isomers should correlate best with σ^- as observed since the removal of the steric congestion during the linkage isomerization allows the rings to assume a coplanar configuration and thereby leads to direct resonance interaction between the nitro group and the tetrazole ring. Further evidence of the conjugated pathway being extended to include the nitro group in the 4-nitro system is found in the UV spectra. A large peak ($\epsilon = 15\,000$–$21\,000$ M^{-1} cm^{-1}) is present in the case of the N2-bonded isomers, which is attributed to the conjugation of the two aromatic rings. The increase in the number of atomic centers in which to delocalize the electrons of 5-(4-nitrophenyl)tetrazole result in a bathochromic shift to a λ_{max} of 296 nm.

The determination of the % N2-bonded impurity also permits the calculation of the absorption spectra of the N1-bonded isomer, which cannot be measured directly. The λ_{max} of the ligand–ligand charge-transfer peak found in the UV spectra of N2-bonded 5-phenyltetrazole complexes undergoes a hypsochromic shift out of the region that can be observed by using nonvacuum techniques in all cases except for the 5-(4-nitrophenyl)tetrazole complex. The peak at $\lambda = 263$ nm arising from the N1-bonded isomer (Figure 1) is due to a charge transfer from the nitro group to the phenyl ring. A similar peak is found in 4-nitrobenzene at $\lambda = 250$ nm in hexane (this difference in λ_{max} is primarily a solvent effect since hexane is a nonprotic solvent).

The k_{3+} values reported in Table III were consistently larger than the corresponding k_{2+} values. Stabilization of the deprotonated complexes in the N1 form through hydrogen bonding involving water and an ammine similar to that found in the nitrito–nitro linkage isomerization[14] is possible. In the protonated complex, such hydrogen bonding would be less likely. The difference in the enthalpies of activation, ΔH^*, for the protonated and deprotonated complexes is approximately 3 kcal/mol in all cases studied. This is consistent with the breaking of a hydrogen bond in the deprotonated complex that is not present in the protonated complex. Solvent-dependent kinetic studies are underway to examine these possibilities. The good fit obtained in the k_{3+} LFER plot indicates the substituents are directly affecting the nucleophilicity of the nitrogen donor atom through electron delocalization. Note that the relative amount of electron density alone is not necessarily an indicator of preferred binding site as

evidenced by the preference of tetrazole complexes for the N2 nitrogen despite the slightly greater nucleophilicity of the N1 nitrogen.[29] Within either the protonated or deprotonated series of 5-(R–phenyl)tetrazole complexes, however, the contributions from steric effects, hydrogen bonding, and other factors should be relatively constant so that the degree of nucleophilicity of the donor atom should directly correlate with the rate of linkage isomerization as observed.

Table VI lists kinetic parameters for other linkage isomerization reactions reported in the literature. All rate constants have been presented for a temperature of 60 °C since that represents the only recorded value for the 4-methylimidazole system.[9] We note that the N-to-N linkage isomerizations reported in this work (Tables II and III) are faster than any of the four other such systems presented in Table VI. If we compare the tetrazolato(–1) systems, the enthalpies of activation are similar for the phenyl-substituted systems of this work and the methyl system of ref 15. However, the entropies of activation are significantly higher for the phenyl systems as might be expected if steric factors were a major driving force for the isomerization since a phenyl ring should experience a greater gain in rotational degrees of freedom (vs a methyl group) upon isomerization from an N1- to an N2-bonded complex. Interestingly, the entropy of activation for the 4-methylimidazolato complex is higher than that for any of the tetrazolato complexes. However, it can be noted that if the 60 °C data point of Table VI in ref 9 is included in the calculation of activation parameters, then values of 26.5 ± 4.0 kcal mol^{-1} and 0.1 ± 11.5 cal deg^{-1} mol^{-1} are obtained for the enthalpy and entropy of activation respectively. While these latter values are more in line with the tetrazolato systems, the rather large error limits involved might just as arguably preclude the drawing of any mechanistic comparisons.

When comparing the protonated tetrazole systems, we once again see a significantly more positive entropic contribution to the isomerization process in the phenyl systems when compared to the methyl system in Table VI, again consistent with steric relief providing a significant driving force for this isomerization. We also note that the enthalpies of activation are higher in the phenyl systems than in the methyl systems, but see no ready explanation for this observation. As with the methyl system, the protonated phenyltetrazole complexes of this work isomerize faster than their deprotonated forms due in large part to ΔH^* values that are lower by 2–4 kcal mol^{-1}. Whether this is due to stronger ground-state bonding for the anionic ligands, solvent participation (perhaps via hydrogen bonds), or significantly different transition states remains unanswered, and studies are underway to examine these possibilities. The 4-methylimidazole system, on the other hand, is significantly *slower* than its deprotonated form. Since, however, the eventual cobalt bonding site must be the protonation site for this system, a slower isomerization rate should not be surprising. This does seem to imply, therefore, that the site of protonation in the N1 tetrazole 3+ systems is not the N2-bonding site.

(29) Takach, N. E.; Holt, E. M.; Alcock, N. W.; Henry, R. A.; Nelson, J. H. *J. Am. Chem. Soc.* **1981**, *102*, 2968.