ring and metal framework. From the results found in this investigation, one concludes that an equivalent internal rotation barrier exists in $Co_2NiCp(CO)_6(\mu_3\text{-}CPh)$. Additional NMR studies are clearly required before any quantitative comparison can be made between the aryl spinning rates in different tetrahedral clusters.

Unlike the phenyl ring, the internal rotation axis of the cyclopentadienyl group is not coincident with the principal axis of the molecular framework. Therefore, the correlation time governing rotation of the Cp's C–H vectors is a somewhat more complex function of θ,[39] $D_\perp$, $D_\parallel$, and R(Cp); $\tau_c = f[\theta, D_\perp, D_\parallel, R(\mathrm{Cp})]$.[40] However, with values of τ_c [from T_1(Cp)], one may still solve the equation[35] for R(Cp). The results are given in the final column of Table II.

One sees that rotation of the Cp group about its C_5 axis is quite facile, with values of R(Cp) somewhat greater than found in the earlier investigation of **1**; e.g. at 298 K, $R(\mathbf{2}) = 50\ \mathrm{ns}^{-1}$ (interpolated) and $R(\mathbf{1}) = 33\ \mathrm{ns}^{-1}$.[8] The rapid internal rotation of the Cp ring provides evidence that there is little or no phenyl/cyclopentadienyl inter-ring interaction. This is not surprising, since the distance of closest approach of protons on the two groups is ~2.3 Å, which is approximately equal to the sum of the van der Waals radii ($2R_H = 2.4$ Å).[41]

Finally, we note that the activation energy determined for R(Cp), $E_a = 1.5$ kcal/mol, is quite similar to that found in **1** (1.6 kcal/mol), and substantially less than the activation energy for R(Ph). This probably results from the fact that, unlike the phenyl ring rotation about its C_2 axis, spinning of the Cp group about its C_5 axis does not require displacement of solvent. Thus, there is less of an intermolecular barrier retarding rotation of the latter ring.

Acknowledgment. We thank the Robert A. Welch Foundation [Grants B-1039 (M.G.R.) and B-657 (M.S.)] and the UNT Faculty Research Program for financial support.

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[39] From the structure,[22] the angle between the Cp axis and the principal axis is $\theta = 99.2°$.

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Solvent Effects on the Linkage Isomerization of the N1-Bonded Pentaamminecobalt(III) Complex of 5-Methyltetrazole

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A study of linkage isomerization for the five-membered cyclic CN_4 tetrazole ligand system from the carbon-adjacent-N1-bonded (5-methyltetrazolato)pentaamminecobalt(III) to its N2-bonded form in 11 different solvents is reported. The solvents include both protic and aprotic solvents as well as the hydroxylic solvents water and methanol. Rate constants in the various solvents were successfully correlated to solvent properties by using Reichardt's acceptor parameter E_T and Gutmann's donor parameter D_N in the equation $\ln k = \ln k_0 + \alpha E_T + \beta D_N$ with $\alpha = 0.0557$, $\beta = 0.0794$, and $\ln k_0 = -18.70$. Alternatively, the equation $\ln k = \ln k_0 + a\alpha + b\beta + c\pi^*$ due to Kamlet and Taft can be used to model the solvent effects. Here α measures the ability of a solvent to act as a hydrogen-bond donor, β measures the solvent's hydrogen-bond-accepting ability, and π^* measures the solvent's dipolarity/polarizability and its ability to stabilize a charge dipole. The fit to these solvent parameters was also successful for all 11 solvents with $\ln k_0 = -17.35$, $a = 0.92$, $b = 2.16$, and $c = 1.98$. These fits are discussed in terms of specific solvent interactions with the complex, and solvent effects on the rate constants for linkage isomerization of the tetrazolato system are compared to solvent effects in the nitrito system.

Introduction

Linkage isomers have drawn a great deal of attention because they enable us to determine which factors are important to the stability of transition-metal coordination compounds and to determine rearrangement mechanisms. Hence, frequent reviews have appeared in the literature.[1] The overall hardness of the metal center as determined by its oxidation state and the hard/soft nature of the other ligands is of primary importance. Hard metal centers are believed to prefer hard donor atoms while softer metal centers will favor softer donor atoms. However, steric effects can also determine which isomer is more stable. When donor atoms are similar or when bulky alkyl or aryl groups are used, the less sterically hindered isomer will be favored. An ever increasing variety of ligands which undergo dynamic linkage isomerization processes have been identified recently, primarily by Jackson and co-workers.[2]

Many studies have been conducted in order to determine the solvent's effect on linkage isomerization reactions. Although electronic effects dominate, the solvent can have a minor influence on isomer stability. It has been found that hard metal centers will coordinate to soft donor atoms in solvents of low dielectric constant but will coordinate to hard donor atoms in solvents of high dielectric constant. Soft metal centers show the opposite effect.[1]

The solvent will also have an impact on the rate of isomerization. This effect can often be modeled successfully on the basis of the solvent's physical and chemical properties. However, in most cases, it is not possible to predict this effect by using only one solvent parameter, and consequently, a multiparameter approach is necessary.[3] In order for the solvent to affect the reaction rate, it must interact specifically with the reacting species. Empirical parameters used to model the solvent effect are direct measures of these interactions. As the number of specific interactions increases, the number of solvent parameters necessary to model the solvent effect will also increase.

Jackson et al. studied the isomerization of $Co(NH_3)_5ONO^{2+}$ to $Co(NH_3)_5NO_2^{2+}$.[4] They showed that the rate of spontaneous isomerization was dependent on two factors. The isomerization is catalyzed by the ability of the solvent to donate electron density to the ammine hydrogens. This weakens the ammine hydrogen

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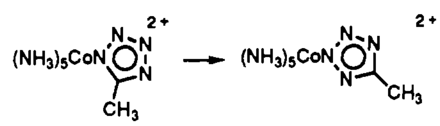
Scheme I



bond, strengthens the ammine–cobalt bond, and weakens the cobalt–nitrito bond. The isomerization is also catalyzed by the ability of the solvent to accept electron density from the anionic nitrito group and thus weaken the cobalt–nitrito bond. They showed that this effect can be modeled successfully by using Gutmann's donor number D_N as a measure of solvent donor ability[5] and Reichardt's acceptor parameter E_T as a measure of the solvent's ability to accept electron density.[6] A good correlation was found for most solvents. However, in the hydroxylic solvents water, methanol, and ethanol the isomerization was significantly slower than predicted by this correlation. This was interpreted as an indication of an intermolecular interaction between the reactant and the hydroxylic solvent. The present study was undertaken to determine if this or a similar interaction might also occur with the (tetrazolato)pentaamminecobalt(III) system, where steric factors rather than electronic factors are believed to be the major driving force for isomerization from the N1-bonded form to the N2-bonded form (shown in Scheme I).

Experimental Section

(1) Syntheses. $[(NH_3)_5CoCl]Cl_2$, $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$, and $[(NH_3)_5CoNCCH_3](CF_3SO_3)_3$ were prepared according to literature procedures.[7,8]

(a) (5-Methyltetrazolato-*N1*)pentaamminecobalt(III) Trifluoromethanesulfonate. $[(NH_3)_5CoNCCH_3](triflate)_3$ (2 grams) was dissolved in a *minimum* (ca. 6 mL) of pH 5.5 acetic acid acetate buffer (1 M buffer). A stoichiometric amount of NaN_3 was added and mixed into the solution. The solution was placed in a scratched 20-mL beaker, which was covered with Parafilm. The solution was allowed to stand overnight at room temperature. The product was collected the next day (ca. 18 h). The crystals were removed and broken over a piece of filter paper in order to absorb residual solution. The product was crushed and dried over a piece of filter paper in order to remove trace nitrile. The yield was approximately 50%. Anal. Calcd for $CoC_2H_{18}N_9(OSO_2CF_3)_2$: C, 9.15; H, 3.45; N, 24.00. Found: C, 9.23; H, 3.50; N, 23.97. Visible and ^1H NMR spectra were identical with those reported for the corresponding iodide salt.[9]

(b) (5-Methyltetrazolato-*N1*)pentaamminecobalt(III) Nonafluoro-1-butanesulfonate. A 1-g sample of $CF_3CF_2CF_2CF_2SO_3K$ (Aldrich), potassium "nonaflate", was dissolved in 15 mL of water under vigorous stirring until the solution was saturated; the mixture was then filtered. A 0.5-g amount of N1-bonded $[(NH_3)_5CoN_4CCH_3](CF_3SO_3)_2$ was finely crushed and dissolved in a minimum of water, and the mixture was filtered. The two solutions were combined and mixed, and the resulting solution was placed on ice for 1 h. The yellow product was collected on a medium frit and dried in a vacuum desiccator.

Solvents. All solvents used were reagent grade or better. Formamide, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylacetamide, acetonitrile, and hexamethylphosphoric triamide (HMPA) were stored over 4-Å molecular sieves for 1 day. *N*-Methylformamide was stored over anhydrous Na_2SO_4 for 1 day. Propionitrile was distilled over P_2O_5 (5 g/L), refluxed over CaH_2 for 1 h (1.25 g/250 mL), distilled, and stored over 4-Å molecular sieves for 1 day. Dimethylsulfoxide (DMSO) was stirred over CaH_2 at room temperature for 5 days (10 g/400 mL). The solvent was distilled under reduced pressure (ca. 10 Torr), and the middle fraction (300 mL) was collected. Anhydrous methanol (MeOH) ($[H_2O] < 0.005\%$) was used without further drying. In-house distilled water was passed through a Universal Model I mixed-resin ion-exchange column supplied by Illinois Water Supply Co.

(2) Kinetic Measurements. For high-solubility solvents (water, DMSO, and carboxamides), approximately 25 mg of N1-bonded $[(NH_3)_5CoN_4CCH_3](CF_3SO_3)_2$ was placed in either a 1- or 2-cm cylindrical UV/vis cell, which was sealed with a wired-down septum. For low-solubility organic solvents, approximately 20 mg of N1-bonded $[(NH_3)_5CoN_4CCH_3](CF_3CF_2CF_2CF_2SO_3)_2$ was placed in either a 2-, 5-, or 10-cm UV/vis cell, depending on compound solubility; the cell was sealed by wiring down Teflon caps after the addition of the required amount of solvent. While the sample was under a N_2 flow, the required amount of solvent was transferred from a sealed solvent bottle to the cell by using a syringe and a 1-μm Gelman Acrodisk CR PFTE filter. The compound was dissolved by vigorously shaking the mixture and/or by placing it for <3 min in an ultrasonic bath. After the compound dissolved, the cell was placed inside a thermostated cell holder in a Cary 17 spectrometer. The absorbance was monitored continuously at 440 nm by using a chart drive. For typical experiments lasting between 12 h and 1 week, error in time was less than 2 min. Temperature was varied between 35 and 65 °C, depending on reaction rate. Most experiments were performed at four different temperatures between 45 and 65 °C. Temperature was maintained to within 0.1 °C. Rate constants were determined by the Guggenheim method using regression analysis or by a Marquardt fit. Activation enthalpies and entropies were determined by a least-squares best fit to a plot of ln (k/T) vs $1/T$. Solvent dependencies were determined by a multiparameter least-squares best fit using the general linear model (GLM) subroutine in the commercial statistics package SAS.

Table I. Activation Parameters and Rate Constants[a] for the Linkage Isomerization of N1-Bonded $(NH_3)_5CoN_4CCH_3^{2+}$

solvent	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$k_{25\,°C}$
DMSO	26.4 ± 0.8	3 ± 2	1.16×10^{-6}
formamide	27.8 ± 1.3	8 ± 4	1.21×10^{-6}
N-methylformamide	27.3 ± 0.1	6 ± 0.1	1.17×10^{-6}
DMF	27.7 ± 0.4	6 ± 1	7.07×10^{-7}
N,*N*-dimethylacetamide	27.3 ± 1.7	5 ± 5	8.24×10^{-7}
N,*N*-diethylacetamide	26.4 ± 0.1	3 ± 0.1	9.23×10^{-7}
CH_3CN	26.0 ± 1.5	-1 ± 4	3.41×10^{-7}
CH_3CH_2CN	26.0 ± 1.3	-1 ± 4	2.59×10^{-7}
HMPA	26.2 ± 0.5	3 ± 2	1.54×10^{-6}
MeOH	28.0 ± 1.6	8 ± 5	8.92×10^{-7}
water	27.1 ± 0.2	5 ± 0.1	1.13×10^{-6}

[a] $\Delta H^\ddagger$ in kcal mol^{-1}, $\Delta S^\ddagger$ in cal K^{-1} mol^{-1}, and k in s^{-1}.

Results

The present work is concerned with the effect of solvent on the N1 to N2 linkage isomerization of $Co(NH_3)_5N_4CCH_3^{2+}$ (see Scheme I). Since many of the organic solvents used in this study absorb appreciably in the ultraviolet region, the visible region was utilized to monitor the kinetics of isomerization. Because the visible spectra of the N1- and N2-bonded complexes do not vary appreciably,[9,10] relatively high concentrations of the N1-bonded complex (typically 0.002–0.02 M) were required for a significant absorbance change. Fortunately, the preparative procedure outlined in the Experimental Section provided a reasonable yield of pure N1-bonded complex as the triflate salt which was free of waters of hydration. The triflate salt proved quite soluble in many of the solvents employed in this study. In those few solvents where the triflate solubility was inadequate, the "nonaflate" salt was employed along with longer path length cells.

Previous work has shown that the linkage isomerization reaction is first order in the N1-bonded complex and essentially irreversible in aqueous media.[10] We have now verified irreversibility in DMSO by ^{15}N NMR studies.[11] Since no anomalously small absorbance changes were observed for the isomerization process in the other nine solvents utilized in this study, complete conversion to the N2-bonded isomer was assumed in these solvents as well. Although the 3+ complex of the protonated tetrazole ligand also undergoes linkage isomerization,[10] none of the solvents utilized in this study are capable of generating kinetically significant amounts of this highly acidic ($pK_a = 1.52$) complex. Isomerization in aqueous media was repeated for this study with no ionic strength control or buffer present to provide experimental conditions compatible with the other solvent systems. Only a slight reduction of the aqueous rate constant from the previously determined value at $I = 1.0$ M was noted.[10] The reaction was followed at elevated

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Table II. Reichardt and Gutmann Solvent Parameters and Rate Constants for the Linkage Isomerization of N1-Bonded $(NH_3)_5CoN_4CCH_3^{2+}$

solvent	E_T	D_N	$\ln k_{exp}$	$\ln k_{calc}$
DMSO	45.0	29.8	−13.67 ± 0.13	−13.83
formamide	56.6	24	−13.62 ± 0.17	−13.65
N-methylformamide	54.1	27	−13.65 ± 0.01	−13.55
DMF	43.8	26.6	−14.16 ± 0.06	−14.15
N,*N*-dimethylacetamide	43.7	27.8	−14.01 ± 0.26	−14.06
N,*N*-diethylacetamide	41.4	32.1	−13.90 ± 0.01	−13.85
CH_3CN	46.0	14.1	−14.89 ± 0.24	−15.02
CH_3CH_2CN	43.7	16.1	−15.17 ± 0.22	−14.99
HMPA	40.9	38.8	−13.38 ± 0.09	−13.35
MeOH	55.5	19	−13.93 ± 0.18	−14.10
water	63.1	18	−13.69 ± 0.03	−13.76

$\ln k_0 = -18.70$, $\alpha = 0.0557$, $\beta = 0.0794$, $\bar{\alpha} = 34.0\%$, $\bar{\beta} = 66.0\%$, $\sigma = 0.12$, $R^2 = 0.97$

$\bar{\alpha} = 100\alpha'/(\alpha' + \beta')$, $\bar{\beta} = 100\beta'/(\alpha' + \beta')$

$\alpha' = |\alpha|(\sum(E_{Ti} - \overline{E_T})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$\beta' = |\beta|(\sum(D_{Ni} - \overline{D_N})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

temperatures and then extrapolated to 25 °C by using ΔH^* and ΔS^*. These rate constants and activation parameters are collected in Table I.

Discussion

For the tetrazolato complex linkage isomerization reported here, the rate constant, k, showed a 5-fold decrease at 25 °C as the solvent was changed from water to propionitrile. This variation in rate constants is substantially less than was found by Jackson et al. for the solvent dependence of nitrate O to N linkage isomerization (43-fold), but is still substantial. Furthermore, if only those solvents common to each study are compared, the rate variation for the nitrito system is only 17-fold. Attempts to measure the rate of tetrazole N1 to N2 isomerization in the "slower" solvents studied by Jackson et al. (ethyl acetate, THF, and 1,2-dimethoxyethane), while desirable, failed due to compound insolubility. It should be noted in this regard that higher concentrations of complex (and/or longer path length cells) were required for this work vis-à-vis the nitrito complex, since absorbance differences between the N1- and N2-bonded tetrazolato complexes are far less pronounced than those in the latter system, where a chromophore change (CoN_5O to CoN_6) is involved.

While the use of multiparameter fits for solvent effects to correlate kinetic processes are common in organic chemistry, few attempts to apply them to inorganic systems have been undertaken. The study of the nitrito to nitro linkage isomerization of pentaamminecobalt(III) complexes by Jackson, Lawrance, Lay, and Sargeson in 1982[4] still represents one of the most thorough studies. A successful fit of their rate constants of isomerization to eq 1

$$\ln k = \ln k_0 + \alpha E_T + \beta D_N \qquad (1)$$

for 12 different solvents was achieved. However, the effect of three hydroxylic solvents (water, methanol, and ethanol) was much slower than predicted by eq 1, and a specific hydrogen-bonding interaction between the hydroxy group of these solvents, the nitrito ligand, and hydrogens of a cis ammine was proposed by the authors to account for these results (see structure 3 on p 1574 of ref 4).

Our results can also be modeled successfully by using Reichardt's acceptor parameter E_T and Gutmann's donor parameter D_N (see Table II).[3] Fitting only our nonhydroxylic solvents as per ref 4, we find a good correlation ($R^2 = 0.97$) to eq 1 with $\alpha = 0.0557$, $\beta = 0.0794$, and $\ln k_0 = -18.70$. If we plot the predicted values versus experimental values (see Figure 1), we find that the data for all solvents (including methanol and water) fit a line with slope = 1. Clearly, we do not find any evidence for a unique, specific intermolecular interaction between hydroxylic solvents and the reactant as was suggested in the nitrito system although a hydrogen-bonding scheme similar to structure 3 of Jackson et al. is possible in the tetrazolato complex system.

Kamlet and Taft have developed a system for analyzing solvent effects which we feel offers many advantages over the traditional acid/base differentiation as characterized by E_T and D_N. Although E_T and D_N have the advantage of being directly measurable, their physical meaning is mixed. Reichardt's parameter E_T is correlated with both the acidic and electronic properties of the solvent.[6,12,13] Gutmann's donor parameter D_N is plagued by the uncertainty of whether to use dilute experimentally measured values or so-called bulk solvent values based on some other correlation.[5,14]

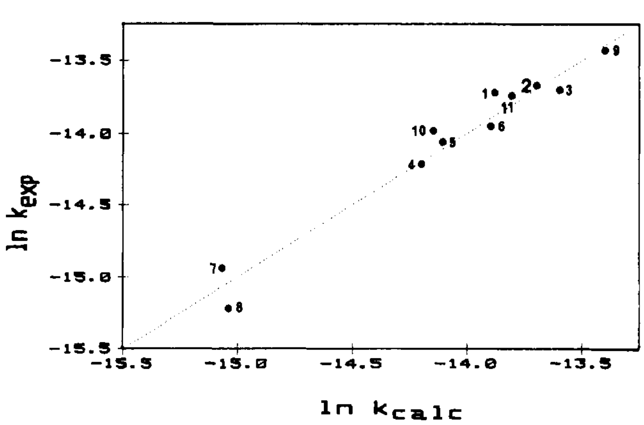

Figure 1. Correlation between experimental and calculated rate constants for the linkage isomerization of N1-bonded pentaamminecobalt 5-methyltetrazolate. The dotted line follows the equation $\ln k_{25^\circ C}(\text{exp}) = \ln k_{25^\circ C}(\text{calc}) = -18.70 + 0.056E_T + 0.079D_N$: (1) DMSO; (2) formamide; (3) *N*-methylformamide; (4) DMF; (5) *N*,*N*-dimethylacetamide; (6) *N*,*N*-diethylacetamide; (7) acetonitrile; (8) propionitrile; (9) HMPA; (10) methanol; (11) pure water.

Kamlet and Taft have attempted to separate solvent effects into three principal components using the solvatochromic comparison method. Their work follows that of Koppel and Palm, who were the first to use a general multiple linear regression analysis to explain solvent effects on rate constants.[15,16] Although these parameters are only approximate, they are as accurate as other solvent parameters and have been determined or can be approximated for many solvents. The first parameter, α, measures the ability of a solvent to act as a hydrogen-bond donor. The second parameter, β, measures the solvent's hydrogen-bond-accepting ability. Finally, π^* measures the solvent's dipolarity/polarizability and its ability to stabilize a charge dipole via its dielectric effect.[17,18]

When the nitrito system is analyzed according to eq 2, one finds a very poor correlation. However, in the hydroxylic solvents,

$$\ln k = \ln k_0 + a\alpha + b\beta + c\pi^* \quad (R^2 = 0.77) \qquad (2)$$

methanol, ethanol, and water, isomerization rates are not significantly slower than predicted. Interestingly, β or the solvent's HBA ability is now not significant (36% chance null hypothesis is correct for the β term). As was found by Jackson et al., if the hydroxylic solvents are deleted, R^2 increases dramatically ($R^2 = 0.90$). However, noncorrelation of hydroxylic solvents is frequently encountered in solvent effect studies and may be due to a high degree of solvent structure.[14] Unless the probe molecule used to determine a specific solvent parameter interacts with the solvent structure in the same way as the complex being studied, it will not correctly predict the solvent effect. The correlation can also be improved by deleting sulfolane ($R^2 = 0.90$) (see Table III). Further improvement can be achieved by deleting additional solvents. Clearly, additional solvent parameters are necessary if we wish to fit all the data points. An attempt was made to use

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Table III. Kamlet and Taft Solvent Parameters and Rate Constants for the Linkage Isomerization of Nitrito-Bonded $(NH_3)_5CoONO^{2+}$

solvent	α	β[a]	π^*	$\ln k_{exp}$	$\ln k_{calc}$	residuals
acetic anhydride	0.00	0.34[b]	0.76	−12.51	−12.06	−0.45
acetone	0.08	0.48	0.71	−12.41	−12.27	−0.14
acetonitrile	0.19	0.37	0.75	−12.13	−11.94	−0.19
1,2-dimethoxyethane	0.00	0.41	0.53	−12.72	−13.35	0.63
DMF	0.00	0.69	0.88	−11.74	−11.39	−0.35
DMSO	0.00	0.76	1.00	−10.60	−10.72	0.12
EtOH	0.83	0.77	0.54	−12.59	−12.51	−0.08
EtOAc	0.00	0.45	0.55	−13.23	−13.24	0.01
formamide	0.71	0.60	0.97	−09.61	−10.22	0.61
MeOH	0.93	0.62	0.60	−12.30	−12.08	−0.22
N-methylformamide	0.36[d]	0.66[b]	0.92[c]	−10.08	−10.83	0.75
pyridine	0.00	0.64	0.87	−11.81	−11.45	−0.36
THF	0.00	0.55	0.58	−13.07	−13.07	0.00
water	1.17	0.18	1.09	−09.45	−09.12	−0.33
sulfolane[a]	0.00	0.42[2]	0.98	−12.94	−10.83	−2.11

$\ln k = -16.31\ (\pm 0.49) + [0.94\ (\pm 0.29)]\alpha + [5.59\ (\pm 0.69)]\pi^*$

$\bar{a} = 27\%,\ \bar{b} = 0,\ \bar{c} = 73\%$

$\bar{a} = 100a'/(a' + b' + c'),\ \bar{b} = 100b'/(a' + b' + c'),\ \bar{c} = 100c'/(a' + b' + c')$

$a' = |a|(\sum(\alpha_i - \bar{\alpha})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$b' = |b|(\sum(\beta_i - \bar{\beta})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$c' = |c|(\sum(\pi^*_i - \bar{\pi}^*)^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$F = 51.8$ (0.0001 confidence level), $\sigma = 0.43$, $R^2 = 0.90$

$F_\alpha = 3.3$ (0.008 confidence level), $F_\pi{}^* = 8.7$ (0.0001 confidence level)

$F_\beta = 0.73$ (0.4823 confidence level based on a three-parameter fit for all solvents except sulfolane)

[a] Not included in correlation analysis (see text). [b] Estimated as $\beta = 0.13 + 0.02D_N$; $\sigma = 0.09$. [c] Estimated as $\pi^* = -0.573 + 14.65(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1)$. [d] Estimated as intermediate between formamide and dimethylformamide.

Table IV. Kamlet and Taft Solvent Parameters and Rate Constants for the Isomerization of N1-Bonded $(NH_3)_5CoN_4CCH_3^{2+}$

solvent	α	β	π^*	$\ln k_{exp}$	$\ln k_{calc}$	residuals
DMSO	0.00	0.76	1.00	−13.67	−13.73	0.06
formamide	0.71	0.60	0.97	−13.62	−13.47	−0.15
N-methylformamide	0.36[c]	0.66[a]	0.92[b]	−13.65	−13.77	0.12
DMF	0.00	0.69	0.88	−14.16	−14.11	−0.05
N,*N*-dimethylacetamide	0.00	0.76	0.88	−14.01	−13.96	−0.05
N,*N*-diethylacetamide	0.00	0.78	0.86	−13.90	−13.96	0.06
CH_3CN	0.19	0.37	0.75	−14.89	−14.89	0.00
CH_3CH_2CN	0.00	0.37	0.71	−15.17	−15.14	−0.03
HMPA	0.00	1.05	0.87	−13.38	−13.36	−0.02
MeOH	0.93	0.62	0.60	−13.93	−13.96	0.03
water	1.17	0.18	1.09	−13.69	−13.72	0.03

$\ln k = -17.35\ (\pm 0.19) + [0.92\ (\pm 0.07)]\alpha + [2.16\ (\pm 0.13)]\beta + [1.98(\pm 0.19)]\pi^*$

$\bar{a} = 34\%,\ \bar{b} = 43\%,\ \bar{c} = 23\%$

$\bar{a} = 100a'/(a' + b' + c'),\ \bar{b} = 100b'/(a' + b' + c'),\ \bar{c} = 100c'/(a' + b' + c')$

$a' = |a|(\sum(\alpha_i - \bar{\alpha})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$b' = |b|(\sum(\beta_i - \bar{\beta})^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$c' = |c|(\sum(\pi^*_i - \bar{\pi}^*)^2/\sum(\ln k_i - \overline{\ln k})^2)^{0.5}$

$F = 143.4$ (0.0001 confidence level), $\sigma = 0.08$, $R^2 = 0.98$

$F_\alpha = 12.5$ (0.0001 confidence level), $F_{\pi^*} = 10.2$ (0.0001 confidence level)

$F_\beta = 16.37$ (0.0001 confidence level)

[a] Estimated as $\beta = 0.13 + 0.2D_N$; $\sigma = 0.09$. [b] Estimated as $\pi^* = -0.573 + 14.65(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1)$. [c] Estimated as intermediate between formamide and dimethylformamide.

the solvent cohesive energy term $\delta_H{}^2$. Since the nitrito isomerization has a negative volume of activation,[4] it was hoped that the reaction rate would be positively correlated with $\delta_H{}^2$. However, $\delta_H{}^2$ appears to be correlated with both α and π^* ($R^2 = 0.90$) and cannot be used with either α or π^*.

In contrast to isomerization rate of the nitrito system, the rate of isomerization of N1-bonded cobalt pentaammine tetrazole can be correlated very well by using α, β, and π^* ($R^2 = 0.98$) (see Table IV). It is interesting to compare the relative importance of hydrogen-bond-donor abilities (HBD), hydrogen-bond-acceptor abilities (HBA), and solvent dipolarity/polarizability for the two systems. Surprisingly, hydrogen-bond-accepting ability is not significant for the nitrito isomerization. Apparently, the energy of the solvent's HBA interaction with the 15 ammine protons is not as strong as previously believed. The dominant factor is the solvent's dipolarity/polarizability. It accounts for 73% of the solvent's effect (see Table III) and must reflect the formation of a well-developed tight ion pair between the pentaamminecobalt moiety and the nitrito anion at the transition state.

Although the solvent's HBA ability is much more important in the tetrazole system, $\bar{b} = 43\%$ (defined in Tables III and IV), the tetrazole isomerization is also much slower than the nitrito isomerization. Therefore, weak solvent HBA interactions with the ammine protons can influence the isomerization rate as suggested by Jackson et al. The π^* parameter is also significant although less important, $\bar{c} = 23\%$ (defined in Tables III and IV). Presumably, the tetrazole system forms a tighter ion pair between the pentaamminecobalt moiety and the tetrazolato anion at the transition state and is affected less by the solvent's dipolarity/polarizability. This difference could be accounted for if the cobalt–tetrazole bond is stronger than the cobalt–nitrito bond and is less susceptible to weakening by the solvent's ability to accept electron density from the coordinated ligand. This is a reasonable and, we believe, correct conclusion.