potentials and the stabilities of the $Fe(HB(pz)_3)_2$ couples are closer to those of $Fe(C_5Me_5)_2$ than to those of the $Fe(C_5H_5)_2$ couples.

Similarities are also evident in the d-orbital energy diagram for D_{5d} $Fe(C_5R_5)_2^+$ and D_{3d} $Fe(HB(pz)_3)_2^+$ shown in Figure 6. In both cases the separation, Δ, between the highest and second highest occupied orbitals is less than the spin-pairing energy.[13,15] This situation must prevail in the 2+ forms, at least for $Fe(C_5Me_5)_2^{2+}$, since the magnetic moment indicates a high-spin configuration. Thus, the first electron to be removed from the neutral complexes is from an a_{1g} orbital and the second is from an e_{2g} $Fe(C_5R_5)_2^+$ or a $1e_g$ $Fe(HB(pz)_3)_2^+$ orbital.

The absorption spectra of the 2+ complexes could yield data concerning orbital energy separations. However, as with other d^4 metallocenes, the band in the spectrum of $Fe(C_5Me_5)_2^{2+}$ centered at 430 nm is probably an unresolved juxtaposition of a number of spin-allowed transitions.[16] The spectrum of $Fe(HB(pz)_3)_2^{2+}$ is unusual in that the blue color of the complex is due to the tailoff of a strong band centered at 833 nm in the IR spectrum; a lower energy shoulder at 1080 nm is also present.

In conclusion, SO_2 has again proven to be a good solvent for electrochemical oxidations. This has allowed the observation of $Fe(C_5H_5)_2^{2+}$, another member of the large, but apparently still growing, group of transition-metal metallocenes, and the production of stable solutions of $Fe(C_5Me_5)_2^{2+}$ and $Fe(HB(pz)_3)_2^{2+}$.

Acknowledgment. Support of this research by the National Science Foundation (Grant CHE 7903729) is gratefully acknowledged.

Registry No. $1^+PF_6^-$, 11077-24-0; 1^{2+}, 86549-93-1; $2^+PF_6^-$, 54182-44-4; 2^{2+}, 75713-66-5; $3^+PF_6^-$, 86549-96-4; 3^{2+}, 86549-94-2; $Fe(C_5H_5)_2$, 102-54-5; $Fe(C_5Me_5)_2$, 12126-50-0; $Fe(HB(pz)_3)_2$, 16949-45-4; SO_2, 7446-09-5.

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Adjacent Methyl to Remote Methyl Isomerization of (4-Methylimidazole)pentaamminecobalt(III)[1]

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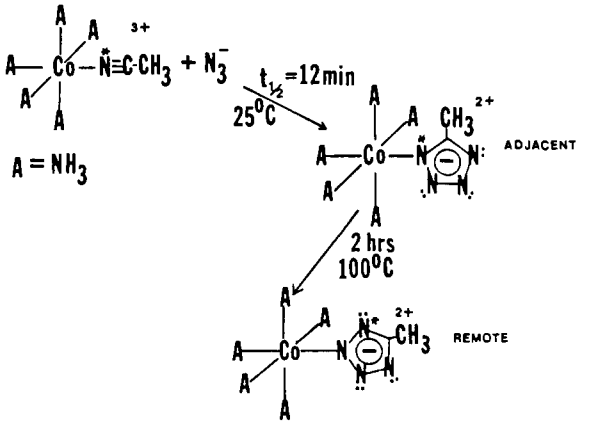
Isomers of (4-methylimidazole)pentaamminecobalt(III) have been isolated as chloride salts with the methyl group of the imidazole directed away from the five NH_3 ligands (remote = R) and near the NH_3 ligands (adjacent = Ad). Isomers have been assigned by a separate X-ray diffraction study. Isomers have been characterized by ^1H NMR spectra showing shifts (ppm) relative to the free ligand (L) as follows: 4-CH_3 Ad = 2.22, R = 2.33, L = 2.27; C_2-H Ad = 7.78, R = 7.88, L = 7.65; C_5-H Ad = 7.08, R = 6.73 (C_4-H), L = 6.77. In Tris or pyridinium buffers two paths are found for the isomerization of Ad to R. One path ($k_0 = (5.83 \pm 2.18) \times 10^{-8}$ s^{-1}) is attributed to the isomerization of the parent 4-methylimidazole species Ad. A second path, first order in [OD^-], is attributed to the imidazolato form Ad_{-H} ($k_{OH} = 3.19 \pm 0.07$ M^{-1} s^{-1}). The activation parameters for the k_{OH} path are $\Delta H^* = 32.4 \pm 4.1$ kcal/mol and $\Delta S^* = 16.8 \pm 11.7$ eu. A mechanism is presented, suggesting a largely dissociative-like transition state. Comparisons are made to the linkage isomerization of $(NH_3)_5Co^{3+}$ coordinated to ONO^- and N_1 of the 5-methyltetrazolato ligand. While the isomerization of the 5-methyltetrazole ligand is faster by 10^5 relative to that for 4-methylimidazole, the anion forms favor the 4-methylimidazolato isomerization by a factor of 400 vs. the 5-methyltetrazolato case. The difference is attributed to different basicity of the lone electron pairs of these ligands. The pK_a's of $(NH_3)_5CoX^{3+}$ have been found at 25.0 °C and $\mu = 0.10$ and are as follows (X, pK_a): imidazole, 9.99; 2-methylimidazole, 10.67; 4-methylimidazole (Ad), 10.46; 4-methylimidazole (R), 10.70. The acid dissociation constants of R and Ad were studied as a function of temperature, yielding values of $\Delta H°$, $\Delta S°$ as follows: (Ad) 17.7 ± 0.5 kcal/mol, 11.2 ± 1.6 eu; (R) 15.4 ± 0.6 kcal/mol, 2.5 ± 1.8 eu. The values of $\Delta H°$ are within a kilocalorie of imidazole's pyrrole pK_a (17.6 kcal/mol) while the values of $\Delta S°$ are more favored by charge dispersal for Ad and R by about 18 to 10 eu, respectively.

Introduction

Ellis and Purcell recently reported the preparation of (5-methyltetrazolato)pentaamminecobalt(III) by the addition of N_3^- across the triple bond of (acetonitrile)pentaamminecobalt(III)[2] as shown in Scheme I.

A slow isomerization ensues from N_1 to N_2 coordination as would be anticipated for removing the strain associated with the adjacent methyl group's interaction with cis-NH_3 ligands.[2,3] A 3.0-kcal strain energy has been calculated from association constants of imidazole and 4,5-dimethylimidazole for $Fe(CN)_5^{3-}$, where ligand repulsions ought to be of similar magnitude.[3] Linkage isomerization reactions between donor atoms of the same kind are much more rare than those between different atoms as in NCS^-, NO_2^-, CN^-, etc., where electronegativity and structural factors provide a driving force for

Scheme I



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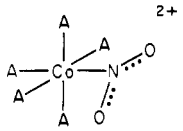
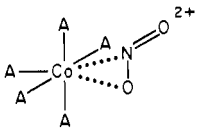
0020-1669/83/1322-2693$01.50/0

the more favored bonding mode. The nitrito to nitro isomerization of $(NH_3)_5Co(NO_2)^{2+}$ is the classic example of the latter class of isomerization reactions. Mechanistic studies have shown that NO_2^- is not released during the isomerization process at the $(NH_3)_5Co^{3+}$ site.[4,5] Jackson et al. reinvestigated this system with isotropic labeling studies which have advanced the π-bonded intermediate (I) as the most likely candidate for



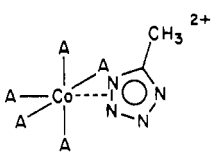
I
A = NH_3

the nitrito-to-nitro isomerization.[6] I differs slightly from the seven-coordinate species, II, which has previously been invoked to account for the absence of incorporation of external NO_2^-.[6]

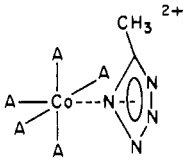


II

The π-bonded intermediate, I, is of interest with respect to isomerization reactions of nitrogen heterocycles such as imidazole,[7] hypoxanthine,[8] and uracil.[9] Purcell has completed the kinetic study for the N_1 to N_2 isomerization of (5-methyltetrazolato)pentaamminecobalt(III).[10] The system shows no evidence for dissociation of the 5-methyltetrazolato ligand during linkage isomerization. Purcell has considered two possible π-bonded intermediates for this process: with Co(III) attached along the N_1–N_2 edge of the ring as in III



III



IV

and with Co(III) perpendicular to the plane of the ring as in IV. The orientation of III is similar to the linkage isomerization intermediate required for $(NH_3)_5Ru(^{14}N^{15}N)^{2+}$,[11] while IV-like structures have been proposed for the isomerization of histidine coordinated to $(CN)_5Fe^{3+}$[12] and for the proton tautomerization between N_1 and N_3 sites of the imidazole ring.[13]

As part of our studies of the complexes of the imidazole series with the transition-metal centers, we had prepared the title complexes, (4-methylimidazole)pentaamminecobalt(III) ($(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$).

Table I. ^1H NMR Resonances in D_2O (ppm)[a]

isomer	4-CH_3	C_2-H	C_5-H
Ad	2.22	7.78	7.08
R	2.33	7.88	6.73
free ligand	2.27	7.65	6.77

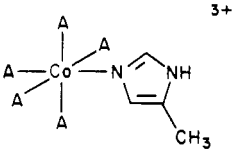
[a] TMPA internal standard at 0.00 ppm.

Table II. Electronic Transition for 4-Methylimidazole and 4-Methylimidazolato Complexes of $(NH_3)_5Co^{3+}$

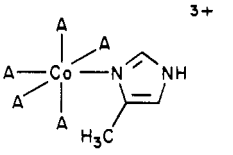
species[a]	conditions	λ(peak), nm (ε)	λ(shoulder), nm (ε)
A_5CoLH^{3+} (Ad)	pH 7.00 (phosphate)	477 (54.5)	
A_5CoLH^{3+} (R)	pH 7.00 (phosphate)	472 (55.5)	
A_5CoL^{2+} (Ad_{-H})	0.5 M NaOH	483 (66.7)	352.5 (101.6)
A_5CoL^{2+} (R_{-H})	0.5 M NaOH	478 (65.1)	348 (99.0)

[a] Abbreviations: A = NH_3; LH = 4-methylimidazole; L^- = 4-methylimidazolate.

We report here the separation of two isomers: remote methyl (R) and adjacent methyl (Ad) coordination as in V and VI. These isomers have been prepared as perchlorates



V = R



VI = Ad

and isolated as chloride salts. As anticipated, a linkage isomerization occurs between the two isomeric forms to produce the more thermodynamically stable product. We report here the kinetic studies which bear on the nature of intermediates during the linkage isomerization.

Experimental Section

$[(NH_3)_5CoOH_2][ClO_4]_3$ was prepared by the literature method.[14a] A 20-g amount (4.3×10^{-2} mol) of $[(NH_3)_5CoOH_2][ClO_4]_3$ and 5 g of 4-methylimidazole (6.1×10^{-2} mol) from Aldrich were heated at 70 °C in dimethyl sulfoxide solvent. The reaction forming $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$ as a mixture of R and Ad was followed spectrophotometrically. The synthetic reaction reaches completion when λ_{max} for the solution becomes 476 nm after 90 min.

Separation of Isomers. The resulting brown solution was diluted to about 1 L with H_2O, allowed to stand for 1 h, and filtered. The filtrate was absorbed on AG50W-X4 cation-exchange resin in the H^+ form (Bio-Rad, 200–400 mesh resin). The resin and absorbed complex was washed with ca. 2 L 1.0 M HCl in 200-mL volumes to remove Co^{2+} contaminants. A 6 M HCl solution was used to elute the isomer mixture of $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$. The eluate was concentrated under reduced pressure of a water aspirator and rotary evaporation at 50 °C until the solution appeared to be turbid. The solution was transferred to a beaker and cooled overnight at room temperature. Solids separate, containing mostly $[(NH_3)_5CoH_2O]Cl_3$ and $[(NH_3)_5CoCl]Cl_2$ with some of the isomer R. This material is discarded, and the solution is further concentrated to give R and Ad as a mixture. Chloride salts of R and Ad were obtained by fractional crystallization from 6 M HCl solution. The Cl^- salts are stable and nonhygroscopic. R is less soluble than Ad. R separates as deep yellow crystals, leaving Ad in the mother liquor, which may be induced to crystallize out by the addition of 95% ethanol in the range 20–40% (v/v). Ad crystallizes as yellow, woollike crystals. Identification and purity of the isomers is best achieved by obtaining NMR and UV–visible data as shown in Tables I and II, respectively, for the separated complexes. It took nearly 30 fractional recrystallizations to obtain pure Ad.

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Spectra. UV–visible spectra of complexes were obtained with use of a Varian-Cary 118C spectrophotometer with solutions in quartz cells. ^1H NMR data were obtained with use of a Varian EM-360 NMR spectrometer with a probe temperature of 30 °C. TMPA (3-(trimethylsilyl)propionic acid sodium salt) served as an internal standard for the D_2O-soluble complexes. D_2O was obtained as 99.8% D from Stohler Isotope Chemicals.

Kinetic Studies. Kinetic measurements for isomerization studies were made with use of the methyl resonances of R and Ad as a function of time. Due to variations in settings which are required for the drift of the EM-360 over the duration of the isomerization process, the mole fraction as determined by the areas under the peak due to a given isomer compared to the total area under both resonances for R and Ad was determined. For accuracy, the areas of the peaks were obtained on an expanded scale. The graph papers containing the time-dependent data were cut out and weighed to determine the total areas and the areas of given isomers. The ratio of the area of a given peak to the total equals the mole fraction of a given isomer at time t. To avoid significant errors introduced in approximating the area of the two isomers, area fractions below 0.35 or above 0.65 were not used in kinetic determinations. The adjacent isomer Ad decreases with time. The rate constants for decay of Ad to R were obtained from a plot of the logarithm of mole fraction of Ad vs. time. Plotting and estimation of the slopes (rate constants) were made with a PDP 11/03 minicomputer.

Sample preparation for the kinetic runs utilized a stock preparation containing an excess of Ad at ca. 0.6 mole fraction. The samples were prepared in D_2O at $[Co(III)]_{total} = 0.20$ M with various buffer salts to control the condition of pD in the sample. The phosphate salt K_2HPO_4 from J. T. Baker and Tris ($(HOCH_2)_3CNH_2$) from Sigma Chemical Co. were used to buffer the sample. The pD was estimated from the reading of pH* from an Orion 601 digital Ionanalyzer standardized with phosphate or borate buffers from Fisher Scientific Co. A combination glass/calomel electrode (Fisher Scientific Co.) was used as the pH probe. In order to determine the appropriate value of the self-ionization constant for D_2O, pK_{D_2O}, the data from ref 14b was utilized in the temperature range 10–50 °C and extrapolated to give values from 50 to 80 °C. A cross-check of the extrapolated values was made by comparing the value of Δ ($=pK_{D_2O} - pK_{H_2O}$) in the range of 10–50 °C where data exists. The value for $pK_{D_2O} - pK_{H_2O}$ was plotted vs. temperature, and the curve was extrapolated into the temperature range 50–80 °C, where a nearly constant difference term of 0.837–0.830 log unit is found. When the correction term found by the extrapolation Δ was added to the known value of pK_{H_2O} in the range 55–80 °C, a second determination of pK_{D_2O} was available. The two determinations were in excellent agreement. Given in respective order, the values of pK_{D_2O} were found to be the following: (55 °C) 13.974, 13.974; (60 °C) 13.850, 13.852; (65 °C) 13.730, 13.733; (70 °C) 13.620, 13.613; (75 °C) 13.510, 13.510; (80 °C) 13.400, 13.409.

The meter readings, pH*, were utilized to evaluate pD in a method analogous to that of Glasoe and Long.[15] The glass/calomel electrode assembly was calibrated with standard aqueous phosphate buffer for which published temperature-dependent values are available throughout the range 25–80 °C. Equimolar amounts (0.100 M) of $H_2PO_4^-$ and HPO_4^{2-} salts were prepared in an ionic strength of 1.20 adjusted with NaCl to match the conditions of ionic strength in the ^1H NMR/kinetic experiments where 0.20 M $(NH_3)_5Co[C_4H_6N_2]Cl_3$ and buffers gave $\mu = 1.20$. Preparation of a $D_2PO_4^-/DPO_4^{2-}$ 0.100 M buffer in D_2O at $\mu = 1.20$ was also done. It was shown that the pK value in D_2O at $\mu = 1.20$ should be corrected from the value in H_2O by the constant -0.13 ± 0.02 for all temperatures in the range 50–80 °C. The correction term of -0.13 ± 0.02 was found to be the same for 0.100 M Tris/Tris-HCl buffer at $\mu = 1.20$ (NaCl); i.e., the correction term is independent of the buffer species involved in the equilibrium as also found by Glasoe and Long.[15]

It was more convenient to record the pH* meter readings at 25.0 °C for the isomerization studies while the conditions of $[OD^-]$ involved in the kinetic processes for isomerization are those at the temperature of the kinetic runs. To evaluate the $[OD^-]$ in a given kinetic experiment, it is necessary to utilize the values of pK_{D_2O} and pD at the kinetic temperature. The value found for pH* at 25.0 °C was changed by the equation $pD = pH^* - 0.13 - T_{cor}$. The term $-T_{cor}$ represents the correction for buffer equilibrium shifts due to measurements in pH* at 25.0 °C vs. the value in a given kinetic experiment. $T_{cor} = 0.00 \pm 0.02$ for phosphate buffer in the range 50–80 °C; the Tris/Tris-HCl buffer pK is much more sensitive to T. Values of T_{cor} for the Tris buffer were found to be the following in D_2O (T (°C), T_{cor}): 80, 1.40; 75, 1.26; 70, 1.17; 65, 1.03; 60, 0.93; 55, 0.83; 50, 0.71; 40, 0.51; 30, 0.13.

The temperatures of the NMR tubes and samples were controlled at a desired temperature with a Haake Type E52 constant-temperature controller immersed in a 10-gal water bath. The samples were held upright within a large test tube filled with H_2O to assure thermal contact with the tubes and glass, while the bulk water bath was continuously circulated to achieve mixing. This assembly allowed placement of a thermometer directly in contact with a set of NMR tubes. Temperature was monitored over time. A maximum fluctuation in T within the supporting large test tube was ±0.3 °C even at the fairly high temperatures needed to study the linkage isomerization of Ad to R. Because removal of a sample tube from the high-T bath could be achieved with a rapid decrease in the temperature to room temperature, where the isomerization process is very slow, NMR measurements could be obtained without altering the apparent "instantaneous" mole fraction. Thus upon a return of the sample tubes tothe high-T bath the isomerization reaction could be resumed from the quenching point on removal from the bath. The total elapsed time was taken to be only the time for the sample tubes at elevated temperature in the bath.

Results and Discussion

Characterization of Complexes. The remote isomer R and the adjacent isomer Ad of $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$ have been isolated as described in the Experimental Section. A crystal of one of the isomers was obtained having the formula $[(NH_3)_5Co(4\text{-}CH_3\text{-}imH)]I_2Cl\cdot 2.5H_2O$. The crystal was cleaved and subjected to an X-ray diffraction study, which established that the isomer of this crystal was of the R form. The structural study will be reported in a future paper.[31] The ^1H NMR spectrum for the R isomer salt was determined *before and after* obtaining the X-ray diffraction data because a period of 4 months had elapsed before the structure was fully determined. The spectra were identical. The chemical shifts for the isomers had been obtained previously as described in the Experimental Section. The chemical shifts of the ^1H NMR resonances are listed in Table I. The isomer matching the R isomer of the crystal study is labeled R; the alternate isomer is specified as Ad.

Previous studies on many heterocyclic compounds of the low-spin d^6 type including $(CN)_5FeL^{3-}$, $(NH_3)_5RuL^{2+}$, and $(CN)_5RuL^{3-}$ as well as several $(NH_3)_5CoL^{3+}$ cases (L = nitrogen heterocyclic ligand) have shown that a substituent placed adjacent to the site of metal coordination has a proton resonance shifted diamagnetically relative to the free ligand, while remote substituents are shifted to higher field.[16-18] Foust and Ford have given a detailed account as to why σ polarization, small paramagnetic contributions, quadrupole effects of metal centers, and back-bonding operate to produce these shift orders for organonitriles and pyridine-type ligands.[17] Similar shifts have been noted for ring ^{13}C resonances of the d^6 low-spin class of compounds.[16]

It is apparent from the data in Table I that *the shift order is not obeyed for 4-methylimidazole complexes of* $(NH_3)_5Co^{3+}$. Indeed, in the absence of the X-ray study one would have assigned the isomers in the opposite sense on the basis of ^1H NMR data alone. However, the structural data conclusively establish the R and Ad assignment as given in Table I. A hydrogen in the C_2 position is shifted diamagnetically for both isomers (0.13 ppm for Ad, 0.23 ppm for R) and is shifted 0.19 ppm for a methyl group of the analogous

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Table III. pK_a's of Imidazoles Coordinated to $(NH_3)_5Co^{3+}$ at 25.0 °C[a]

ligand	pK_a	ligand	pK_a
imidazole	9.99	4-methylimidazole (Ad)	10.46
2-methylimidazole	10.67	4-methylimidazole (R)	10.70

[a] Recorded at $\mu = 0.10$.

2-methylimidazole complex of $(NH_3)_5Co^{3+}$.[19] If the CH_3 or H substituent is adjacent to the Co(III) center at C_4 as in the Ad or R isomer, respectively, a small paramagnetic shift is observed for the 4-methylimidazole complex: CH_3 by 0.05 ppm and H by 0.04 ppm. For the remote CH_3 or H position in R or Ad, respectively, both isomers exhibit diamagnetic shifts relative to the free ligand: 0.06 ppm for CH_3, 0.31 ppm for H.

It appears that, for the imidazole ring coordinated to $(NH_3)_5Co^{3+}$, σ polarization and inductive effects are more prominent at the remote (C_5) position than has been observed with the resonance shifts for substituents at approximately equal distances to the Co(III) center in complexes of other N heterocycles. The C_2 position appears to be influenced by σ effects from Co(III) and by the two adjacent ring N atoms. The small paramagnetic shift observed for the methyl or hydrogen adjacent to Co(III) at C_4 in the 4-methylimidazole complex is difficult to interpret. It is probably due to a field influence or a specific interaction with the metal center.[34] However, we have carried out the preparation of 1,4-dimethylimidazole and 1,5-dimethylimidazole complexes of $(NH_3)_5Co^{3+}$.[35] In this system the site of N_1 is blocked by methyl and the adjacent and remote positions, C_4 and C_5, become fixed. The ^1H spectra exhibit diamagnetic shifts of 0.03 ppm for CH_3 and 0.15 ppm for H at C_4 and diamagnetic shifts of 0.17 ppm for CH_3 and 0.17 ppm for H at C_5. Thus, the position of the ^1H resonance for a C_4 substituent varies from complex to complex under the influence of factors that are difficult to assess independently of each other.[34] It should be noted that the N-heterocyclic complexes of $(CN)_5FeL^{3-}$, $(NH_3)_5RuL^{2+}$, $(CN)_5RuL^{3-}$, and $(CN)_5CoL^{2-}$ have not been examined for hindered substituents such as CH_3 in the 2-position of pyridine rings while the 4-methylpyridine CH_3 resonance is found to be diamagnetically shifted, even though it is remote.[16]

The important result is that the trends that have been observed in the ^1H spectra of other low-spin d^6 complexes may not be used to establish structure assignments for coordination of the tautomeric forms of imidazoles. The results of ^{13}C shifts are also different from the trends that have been noted previously.[16] The ^{13}C spectra will be reported together with the structural results for these complexes.[31]

When the pH of the sample is raised above 10.0, the equilibrium shown in eq 1 shifts to the right, producing the

$$\underset{\text{R or Ad}}{(NH_3)_5CoLH^{3+}} + OH^- \rightleftharpoons \underset{\text{R}_{-H}\text{ or Ad}_{-H}}{(NH_3)_5CoL^{2+}} + H_2O \quad (1)$$

coordinated 4-methylimidazolato complex from the respective isomer of the parent complex R or Ad. The electronic spectra of the remote and adjacent isomers differ in the position of the maximum of the electronic transition. The remote isomer's electronic transition occurs 222 cm^{-1} higher in energy than that of the adjacent isomer. The values shown in Table II are typical for the $Co^{III}N_6$ environment; the transition for $Co(NH_3)_6^{3+}$ occurs at 473 nm for comparison.[20] When isomers R and Ad are deprotonated in 0.50 M NaOH, new electronic transitions for R_{-H} and Ad_{-H} are observed as recorded in Table II. The extinction coefficients for all species in Table II are characteristic of the d–d transition of Co(III) pentaammine complexes.

Table IV. Temperature Dependence of the Acid Dissociation Constant of Ad and R Isomers[a]

	pK_a			pK_a	
T, °C	Ad	R	T, °C	Ad	R
25.0	10.46	10.70	65.0	8.87	9.41[b]
35.0	10.05	10.37	70.0	8.67[b]	9.20
40.0	9.85[b]	10.18	75.0	8.47[b]	9.06[b]
50.0	9.50	9.91	80.0	8.27[b]	8.95
60.0	9.09	9.62			

[a] Conditions: $\mu = 0.12$; pH standardized vs. borate buffers at T, $[Co(III)]_{total} = 0.0200$ M; [acid form] = [base form] = 0.0100 M. [b] Interpolated data points.

The pK_a's of a series of imidazole complexes for $(NH_3)_5Co^{3+}$ are given in Table III. These values were obtained by potentiometric titration of the respective $(NH_3)_5CoLH^{3+}$ complexes, which were prepared by procedures analogous to that for the 4-methylimidazole derivative. The pK_a of the imidazole complex itself has been reported by Harrowfield et al. at 10.0,[21] which is observed to be in excellent agreement with our result. When the ring methyl substituent is adjacent to pyrrole hydrogen in the case of the 2-methylimidazole complex or isomer R, the pK_a is essentially the same, 10.69 ± 0.02. Inclusion of the methyl substituent increases the basicity of the pyrrole position for the 2-methylimidazole complex and either R or Ad. When Ad is titrated, its pK_a is found to be lower than that of the remote isomer R. This may be due to a slight influence of induction from an electron-releasing methyl group near the site of deprotonation. One would anticipate that the basicity of R would have to be greater than for Ad on the basis of donation of a methyl group through the σ-bond system.

The temperature dependence of the pK_a's of the R and Ad isomers were examined with use of the 50:50 buffer point with 1.00×10^{-2} M of the imidazole and imidazolate form. Results are given in Table IV. Although K_a changes with temperature, the extent of the shift in equilibrium is not sufficient to change the analytical concentrations of the R/R_{-H} and Ad/Ad_{-H} pairs. An isomerization process for the Ad isomer complicates the obtainment of data at higher temperatures due to the equilibrium time required to standardize the glass electrode vs. borate buffer in the proper temperature range. Therefore, fewer points were obtained for the Ad isomer. A plot of log K_a of either isomer vs. $1/T$ is an excellent straight line, which allows for interpolation of data in the desired range where the isomerization takes place. The isomerization reaction will be described in the next section.

The data in Table IV were treated by the standard $-\log K$ vs. $1/T$ plot to yield standard enthalpies and entropies for the R and Ad forms for reaction 2. The values were found as

$$(NH_3)_5CoLH^{3+} + H_2O \rightleftharpoons H_3O^+ + (NH_3)_5CoL^{2+} \quad (2)$$

follows: Ad, $\Delta H° = 17.6 \pm 0.5$ kcal/mol, $\Delta S° = 11.2 \pm 1.6$ eu; R, $\Delta H° = 15.4 \pm 0.6$ kcal/mol, $\Delta S° = 2.5 \pm 1.8$ eu.

Adjacent to Remote Isomerization. In solution Ad converts with time to R. The reaction proceeds to completion of the limit of detection, <5% Ad. This is shown in Figure 1a with a representative set of spectra for the methyl region starting with a 65:35 mixture of Ad:R at the normal sweep width of 10.0 ppm. With time the methyl resonance of Ad decreases as the amplitude of the remote isomer R increases. A corresponding change occurs for the C_4–H resonances; however, the sensitivity for following the change is too low with this

(19) Johnson, C. R. Ph.D. Dissertation, University of Pittsburgh, Pittsburgh, PA, 1982.
(20) This work; λ_{max} was invariant from 0.10 M HCl to 0.50 M NaOH.
(21) Harrowfield, J. M.; Norris, V.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 7282.

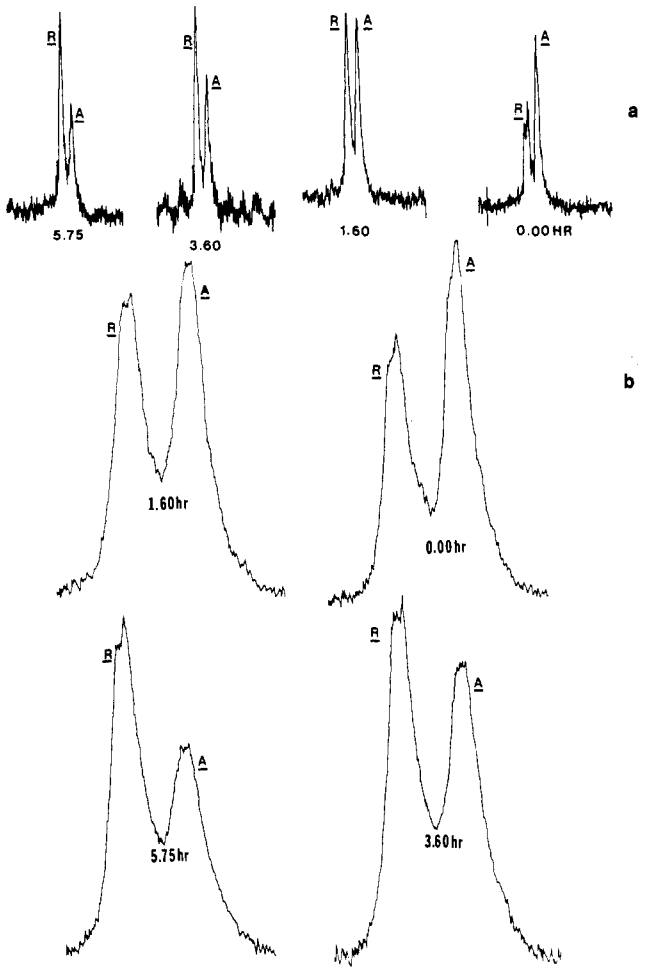


Figure 1. Methyl region of ^1H NMR spectra at pD 9.02 and 80.0 °C for R to Ad isomerization: (a) sweep width 10.0 ppm; (b) sweep width 1.00 ppm. [Tris] = 0.20 M; [R + Ad] = 0.20 M. In this figure, R and Ad stand for the remote (R) and adjacent (Ad) isomers, respectively.

Table V. Rates of Isomerization at 60 °C in Amine Buffers

pH at 25 °C	pD_{cor} at 60.0 °C	$10^7[OD^-]$,[a] M	10^6k, s^{-1}
5.10[b]	4.38	0.00340	0.055
7.45	6.39	0.347	0.200
8.12	7.06	1.62	0.540
8.70	7.64	6.17	2.03

[a] Calculated at 60 °C with pK_{D_2O} = 13.85, Tris buffer. [b] Pyridine/pyridinium buffer.

resonance. The kinetic aspects of the isomerization process were followed at the methyl resonance as described in the Experimental Section. The graphical evaluation of the area was carried out at a sweep width of 1.00 ppm. The appearances of the same solutions as in Figure 1a are shown in Figure 1b for the expanded scale. When the pD of the NMR tube solution was maintained with nonanionic buffer systems, the results for the rate of isomerization at 60 °C were as shown in Table V. These solutions were controlled in pD with the pyridine/pyridinium ion buffer or Tris buffer system having aqueous pK_a's at 5.31 and 8.08 at 25.0 °C, respectively.[22] A run of three samples at the same pD value of 8.21 gave a value reproducible to ±7.4% of (0.67 ± 0.05) × 10^{-6} s^{-1} in Tris buffer, also at 60 °C. These representative experiments establish the reproducibility of the other rates, which were determined for only one run each. The data in Table V correlate with the rate law in eq 3. The values of k_0 and k_{OH^-} are found

$$k_{obsd} = k_0 + k_{OH^-}[OH^-] \quad (3)$$

to be (5.83 ± 2.18) × 10^{-8} s^{-1} and 3.19 ± 0.07 M^{-1} s^{-1}, respectively.

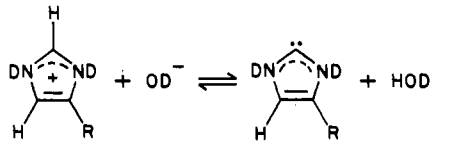
Table VI. Temperature Dependence of the Ad to R Isomerism in 0.20 M Amine Buffers

T, °C	pD_{cor}	$10^7 \times [OD^-]$, M	10^6k_{obsd}, s^{-1}	pK_{D_2O}	10^5f,[a] s^{-1}
60.0	7.28	2.69	0.74	13.85	3.54
65.0	7.16	2.69	1.18	13.73	4.30
70.0	7.04	2.63	2.14	13.62	6.77
75.0	6.94	2.69	7.75	13.51	19.5
80.0	6.84	2.75	15.40	13.40	30.8

[a] $f = (k_{obsd}/[OD^-])(K_{D_2O}/K_{a(CoA_5LH^{3+})})$; μ_{total} = 1.4.

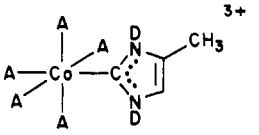
The rates of isomerization for the Ad to R process were studied as a function of temperature. The results are given in Table VI.

Exchange of C_2–H for D. It is known that imidazoles as free ligands undergo a deuterium-exchange reaction in D_2O at the C_2 position as shown in eq 4.[24,25] As the ylide form



(4)

of imidazole is incorporated into the product during isomerization of N_1 to C_2 with $(NH_3)_5Ru(imH)^{2+}$ and its derivatives,[7] it seems reasonable to ask if this form could be involved in the isomerization of Ad. The integration of the C_2–H and C_5–CH_3 resonances of Ad were monitored at pD 8.87 in phosphate buffer at 60.0 °C. A sample of 4-methylimidazole also at pD 8.87 (phosphate) and 60.0 °C was prepared. Immediately after mixing the integration ratio of the C_5–CH_3 to C_2–H resonance was 3.06 (theoretical value 3.00). The integration ratio of the isomer mixture increased to 4.00 at 48 h and 4.22 in 72 h. Under the same conditions the C_2–H resonance of the free ligand had vanished in 72 h. The C_4–H resonance ratio was initially 3.00 and was measured as 3.13 (virtually unexchanged) in 72 h. The total area for the C_4–H resonance of R and Ad compared to that for C_5–CH_3 was 2.96 at 48 h (no exchange at C_4 for the coordinated ligand). Therefore, only the C_2–H position of the coordinated ligand undergoes D exchange during the time for the isomerization of Ad to R. The amount of exchange is implicated by the integration ratios in 25.0 ± 8.3% at 48 h and 29.1 ± 8.3% at 72 h. During the same interval the isomerization reaction becomes 80% complete (72 h). This provides an important consequence for the isomerization process in D_2O. The pD dependence establishes that the most efficient path is via the imidazolato form of the complex (discussed in detail below). However, if VII or its



VII

imidazolato form had been an intermediate in the isomerization reaction, then every conversion of Ad to R would yield

(22) Sillen, L. G.; Martell, A. E. *Spec. Publ.—Chem. Soc.* **1964**, *No. 17*.
(23) Kingerley, R. W.; LaMer, V. K. *J. Am. Chem. Soc.* **1941**, *63*, 3256.
(24) (a) Noszal, B.; Schellec-Krattinger, V.; Martin, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 1078. (b) Sundberg, R. J.; Martin, R. B. *Chem. Rev.* **1974**, *74*, 471.
(25) (a) Haake, P.; Bausher, L. P.; Miller, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1113. (b) Haake, P.; Bausher, L. P. *J. Phys. Chem.* **1968**, *72*, 2213.

exchange of the C_2–H position in D_2O. This is not the case; exchange of D at C_2 is 2.7 times slower than the isomerization of Ad at 60.0 °C. Rowan, Storm, and Rowan have reported that the imidazole complex, $(NH_3)_5Co(imH)^{3+}$, shows no detectable exchange at C_2 at pH 8.1 and 44 °C.[26] These conditions are 8-fold lower in $[OD^-]$ and 16 °C lower than our conditions, and it is therefore reasonable that our data would show the higher rate of exchange at the C_2 position. In fact, at pD 8.21 and 60.0 °C we have observed 7.0% exchange in 85.3 h, intermediate in both conditions and amount of exchange of our mentioned study and of ref 26. In the same interal Ad to R isomerization had proceeded to 50% completion, isomerization being approximately 7 times greater than exchange at C_2. Hence VII can be ruled out as a potential intermediate, and presumably its precursor analogue of III can also be rejected. This seems reasonable in that $(NH_3)_5Co^{3+}$ is a relatively hard metal center in contrast to the soft center with $(NH_3)_5Ru^{2+}$, where a species like VII is known to exist. Co(III) is far less likely to interact favorably with antibonding levels of the ylide structure of imidazoles; Ru(II) would have this capacity.

It should be noted that although exchange occurs for C_2–H at a rate reduced from that of the free ligand under the same conditions, it is not surprising the complex undergoes exchange at C_2–H. The rate law for exchange of the free ligand requires deprotonation of the C_2 position.[24,25] Although the concentration of the ylide form of the free ligand cannot be measured, it is still the kinetically active one and is stabilized by resonance. The C_2–H pK_a of imidazole is estimated as 32.5. Coordination of an imidazole influences the pK_a of the pyrrole position by increasing its acidity by 4.4 log units. It is reasonable that Co(III) can enhance the acidity of the C_2–H position via an even stronger σ induction over the shorter distance to the metal center for C_2–H vs. pyrrole N–H. This should accelerate the C_2–H exchange reaction. That the observed result is a suppression in rate, even though C_2–H should be more acidic, must be attributed to a loss of resonance stability of the ylide form when Co(III) resides at one of the ring nitrogens and either D or H at the other.

Mechanism of Adjacent to Remote Isomerism. The linear dependence of the isomerization rate constant according to eq 3 suggests parallel routes to the R isomer according to eq 5–8. The rate law consistent with eq 5–8 is eq 9. The data

$$\mathrm{Ad} \overset{K_a}{\rightleftharpoons} \mathrm{Ad_{-H}} + \mathrm{H_3O^+} \tag{5}$$

$$\mathrm{Ad} \xrightarrow{k_0} \mathrm{R} \tag{6}$$

$$(\mathrm{Ad_{-H}}) \xrightarrow{k_1} (\mathrm{R_{-H}}) \tag{7}$$

$$(\mathrm{R_{-H}}) + \mathrm{H_3O^+} \rightleftharpoons \mathrm{R} + \mathrm{H_2O} \tag{8}$$

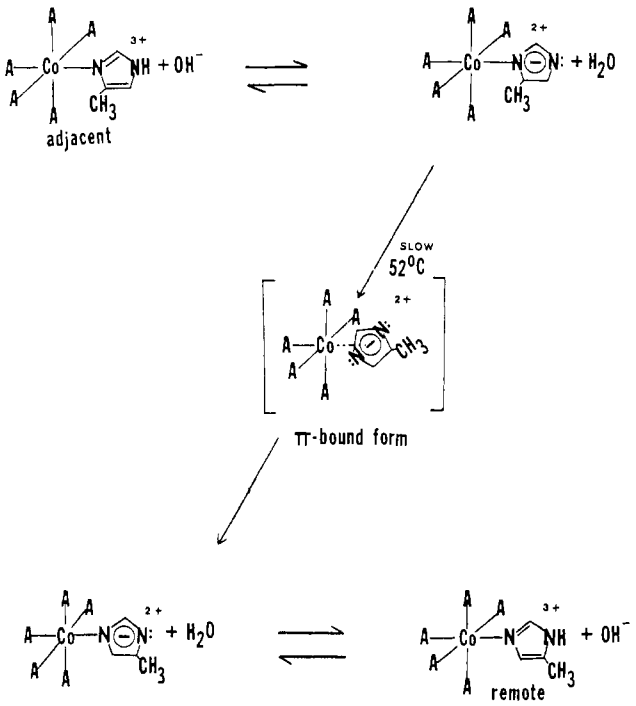
$$\frac{d[R]}{dt} = \frac{k_0 + \dfrac{k_1 K_a}{[H_3O^+]}}{1 + \dfrac{K_a}{[H_3O^+]}}[Ad] \tag{9}$$

in Table V show that for any pD < (pK_a − 1), the denominator term in eq 9 approaches 1.0; eq 9 can then be rewritten, yielding the value of k_{obsd} as in eq 10. For the amine buffer

$$k_{obsd} = k_0 + \frac{k_1 K_a}{K_w}[OH^-] \tag{10}$$

group $k_0 = (5.83 \pm 2.18) \times 10^{-8}$ s^{-1} and k_1 is calculated to be 9.6×10^{-4} M^{-1} s^{-1} for the path involving the imidazolato

Scheme II



ligand at 25.0 °C. The ruling out of VII as a possible intermediate, together with the fact that isomerization takes place without loss of the 4-methylimidazole to any measurable extent, implies that the imidazole and imidazolato rings are retained in the coordination sphere and solvent cage of $(NH_3)_5Co^{3+}$. At pH 8 the imidazolato pathway is 55-fold more efficient than the intrinsic path for the neutral imidazole to undergo the isomerization. It should be noted that imidazole undergoes its tautomerization by several paths.[27] The neutral molecule inside a water solvent cage tautomerizes at 1.4×10^6 s^{-1}. Coordination by $(NH_3)_5Co^{3+}$ reduces the tautomerization process by 2.4×10^{13} as one might anticipate if the rate-limiting step involves Co^{III}–N bond rupture instead of N–H bond rupture. The case of H tautomerization between N sites in imidazole rings might be viewed as a conducted-tour mechanism of H^+ with solvent participation to stabilize the separation of charge. Since the k_0 path is observed kinetically and there are no readily available lone pairs on the coordinated imidazole ring that are adjacent to the bonding N, the isomerization of Ad to R by the k_0 path would seem to be very similar to the conducted-tour tautomerization of the imidazole ring—only in this event the $(NH_3)_5Co^{3+}$ moiety must remain associated with the π cloud of the imidazole ring as a proton migrates within a solvent cage to complete the linkage isomerization.

The influence of OH^- on catalyzing the rate is consistent with the steps shown in Scheme II, with OH^- deprotonating the most acidic site in the $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$ complex.

In the case of the imidazolato form of the ligand, a site having an available lone pair exists even if it is three bonds remote (across the ring). The π-bound orientation of the intermediate is the same as that proposed here for the neutral-ligand isomerization path, without a proton on the opposite π face. The π-bound form is similar to the intermediate proposed by Jackson, Lay, and Sargeson for the isomerization of $(NH_3)_5Co(NO_2)^{2+}$ (see structure I).[6] Indeed, migration across the three-atom bridge N_1–C_2–N_3 is similar to the case for I and such a contact would avoid some crowding of the amines of $(NH_3)_5Co^{3+}$ and the 4-methyl position. The π-bound intermediate would be similar to the half-sandwich

(26) Rowan, N. S.; Storm, C. B.; Rowan, R. *J. Inorg. Biochem.* **1981**, *14*, 59.

(27) (a) Reference 13. (b) Eigen, M.; Hammes, G. G.; Kustin, K. *J. Am. Chem. Soc.* **1960**, *82*, 3482.

Table VII. Rates and Activation Barriers for Linkage Isomerizations of Anionic Ligands

system	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_1, s^{-1} (conditions)	ref
$(NH_3)_5Co(4\text{-}CH_3\text{-}im)^{2+}$ (Ad_{-H})	32.4 ± 4.1	16.8 ± 11.7	3.5×10^{-5} (pD 7.28, μ = 1.40, 60 °C)	this work
$(NH_3)_5Co(5\text{-}CH_3CN_4)^{2+}$ (N1)	26.0 ± 1.8	2.5 ± 5.6	4.2×10^{-4} (μ = 1.0, 65 °C)	10
$(NH_3)_5CoNO_2^{2+}$	22	−5	2.93×10^{-3} [a]	5
	22.7 ± 0.8	−0.8 ± 0.8	8.13×10^{-3} [a]	6

[a] Calculated at 60 °C.

complex of benzene (Bz) as recently prepared in $RuBz(H_2O)_3^{2+}$ and $OsBz(H_2O)^{2+}$;[28] however, the bonding would be weaker in competition with five strong σ donors of $(NH_3)_5Co^{3+}$ than for the Ru(II) and Os(II) cases cited, where π affinity for the aromatic benzene ring would be large. The imidazolato π-bonded intermediate for isomerization of Ad to R would be much more ionic in character due to the increased electronegativity of N atoms relative to C of benzene. A closer analogy for the π-imidazolato coordination would be cyclopentadienide, Cp^-, in half-sandwich compounds. Such a π complex is a logical intermediate of less stability than either R or Ad, but kinetically important. The absence of directly adjacent lone pairs for isomerization of Ad_{-H} is in contrast to the case of the (5-methyltetrazolato)pentaammminecobalt(III) N_1 to N_2 isomerization. Hence, it would appear that III is a good candidate for that process while the equivalent of IV operates for the title complex.

A comparison of the linkage isomerization of the 4-methylimidazolato, 5-methyltetrazolato, and nitrito anions is given in Table VII. The activation parameters for the isomerization via the imidazolate form of the complex were obtained from the data in Table VI. Since the hydroxide-dependent component of the rate law is much larger than the k_0 contribution, the value of k_{obsd} is approximately $(k_1K_a/K_{D_2O})[OD^-]$. The values of k_1 were calculated by using the data for pK_{D_2O} and pK_a of the Ad isomer from Table IV (corrected by −0.13 for the change to D_2O solvent) and the pH* measurement of $[OD^-]$ for the range of 60.0–80.0 °C. The values of k_1 are shown as f in Table VI. When k_1 is treated by the Eyring relationship, the plot of $-\ln(k_1/T)$ vs. $1/T$ yields the values of $\Delta H^{\ddagger}$ = 32.4 ± 4.1 kcal/mol and $\Delta S^{\ddagger}$ = 16.8 ± 11.7 eu.

Purcell's study of the tetrazolato system has revealed three isomerization pathways: one at high $[H_3O^+]$ for the protonated ligand complex $(NH_3)_5Co(CH_3CN_4H)^{3+}$, one for the anionic ligand complex $(NH_3)_5Co(CH_3CN_4)^{2+}$, and an S_N1CB path at high $[OH^-]$. Only two of these are found for the isomerization of $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$. With the 5-methyltetrazolato ligand no additional acidic proton is present on the ring. The $[OH^-]$-dependent path at $[OH^-] > 0.10$ M for $(NH_3)_5Co(CH_3CN_4)^{2+}$ is also found as a kinetic path for isomerization of $(NH_3)_5CoNO_2^{2+}$.[6] In each of these cases the $[OH^-]$-dependent path is attributed to an S_N1CB-catalyzed isomerization. Deprotonation of NH_3 ligands is well-known to enhance the substitution lability of $(NH_3)_5CoX^{2+}$ salts (X = a common anion such as Cl^-). The distortion of the $(NH_2)(NH_3)_4CoX^+$ intermediate and π-bonding of the NH_2^- ligand to Co(III) apparently suffices to weaken the Co^{III}–N bonds toward isomerization of the O to N migration with NO_2^- and N_1 to N_2 migration of the 5-methyltetrazolato ligand.

A base-catalyzed decomposition of the title complex occurs at high $[OH^-]$. The slow isomerization reaction of Ad to R precluded studies at high $[OH^-]$. In addition, as the percent of imidazolato forms R_{-H} and Ad_{-H} increases relative to that of R and Ad, the chemical shifts of the methyl resonances approach each other more closely. Therefore at high $[OH^-]$, the graphical method will not be suitable to follow the linkage isomerization even if competitive loss of NH_3 and imidazole were not a problem. Hence we have not studied the isomerization of Ad under conditions where an S_N1CB-active path is detected for $(NH_3)_5Co(CH_3CN_4)^{2+}$ or $(NH_3)_5CoNO_2^{2+}$. The isomerization of the title complex is different from these cases in that the coordinated imidazole possesses an acidic pyrrole hydrogen (cf. Tables III and IV). The $[OH^-]$-dependent path for the Ad to R isomerization shows the first-order dependence in $[OH^-]$ at much lower $[OH^-]$ than is kinetically important for deprotonation of an NH_3 ligand. Rather the imidazolato form as shown in Scheme II is induced by OH^-. In Purcell's study[10] the activity of the $[H_3O^+]$-dependent path for $(NH_3)_5Co(CH_3CN_4H)^{3+}$ is analogous to the k_0 path of eq 5. In both cases the neutral ligand, 5-methyltetrazole or 4-methylimidazole, undergoes linkage isomerization although the 5-methyltetrazole ligand has extra lone pairs to accommodate the proton readily. The imidazole case requires the conducted-tour orientation of $(NH_3)_5Co^{3+}$ and H^+ over an imidazolato-like intermediate. To compare the $[H_3O^+]$-dependent path for $(NH_3)_5Co(CH_3CN_4)^{2+}$ vs. the k_0 path of $(NH_3)_5Co(4\text{-}CH_3\text{-}imH)^{3+}$ requires determining the rate of the former under conditions where $(NH_3)_5Co(CH_3CN_4H)^{3+}$ is fully formed. Using the activation parameter data of Purcell,[10] we calculate the linkage isomerization of the 5-methyltetrazole ligand on $(NH_3)_5Co^{3+}$ as 8.1×10^{-3} s^{-1} compared to 5.83×10^{-8} s^{-1} for Ad and 2.9×10^{-3} s^{-1} for $(NH_3)_5CoNO_2^{2+}$, where no HNO_2 path is observed. One can see that the NO_2^- and 5-methyltetrazole rates are comparable but that the 4-methylimidazole path (eq 5) is slower by about 10^5. The imidazole ligand is more basic than the tetrazolato anion by 1.6 pK units. In a comparison of equivalent neutral ligands, the imidazoles would be much stronger bases than the tetrazoles and should make a stronger σ-bond. This is shown in the activation enthalpies of the comparison of anion forms in Table VII. As bases, the imidazolato ligands are stronger bases toward external protons by about 9.0 pK units (ref 10 and this work). The extra-electron-rich nature of the imidazolato form can in turn serve as a stronger internal σ donor toward Co(III). The effect is a 6.4 kcal/mol greater cost to rupture the Co^{III}–N bond of Ad_{-H} than for the tetrazolato case. The activation enthalpies of both linkage isomerizations for imidazolato and tetrazolato ligands are positive and probably represent an expansion of volume for the activated complex. The activation parameters for isomerization of Ad_{-H} are very close to the dissociation activation parameters of N_3^-.[29] Note that both are anionic N-bonded ligands. The literature values for the dissociation activation parameters of N_3^- are $\Delta H^{\ddagger}$ = 34 kcal/mol and $\Delta S^{\ddagger}$ = +14 eu.[29] These values support the conclusion that the linkage isomerization of Ad_{-H} is very similar in nature to a dissociative or bond-breaking reaction. The larger $\Delta S^{\ddagger}$ for the 4-methylimidazolato case may also point to different geometries for these linkage isomerization reactions as described above. Under conditions where the 4-methylimidazolato complex is fully formed, 2 pK units above

(28) Hung, Y.; Kung, W.; Taube, H. *Inorg. Chem.* **1981**, *20*, 457.

(29) Lalor, G. C.; Moelwyn-Hughes, E. A. *J. Chem. Soc.* **1963**, 1560.

(30) (a) Reference 12. (b) A related effect of unhindered to hindered coordination for the dissociation of histidine and 4-methylimidazole has been observed for the Fe(III) analogue by S. O'Donnell in our laboratory.

(31) Henderson, W.; Mott, G.; Hoq, M. F.; Shepherd, R. E., to be submitted for publication.

10.46, a rate of 0.13 is calculated at 60 °C from the amine buffer data. The corresponding rate for the 5-methyltetrazolato complex is calculated to be 3.1×10^{-4} s^{-1}, and that of the NO_2^- complex is 2.9×10^{-3} s^{-1}. Hence although the neutral ligands show a 10^5 advantage for 5-methyltetrazole, which has additional lone pairs to accommodate proton migration, for the anionic species the imidazolates are faster by 2-3 orders of magnitude. In comparison with the tautomerization of H^+ around the "imidazolate" ligand and that of $(NH_3)_5Co^{3+}$ a rate reduction of 1×10^7 is detected for the bulky group, but this path is still 2×10^6 faster than when both $(NH_3)_5Co^{3+}$ and H^+ must migrate in some concerted fashion.

Driving Force of the Linkage Isomerization. One is left with the question of the driving force of the Ad to R linkage isomerization. From the results using 5-methyltetrazolate as the ligand for $(NH_3)_5Co^{3+}$, the steric factor would favor isomer R thermodynamically. The influence of steric interaction may be estimated as about 3.0 kcal/mol.[3] The steric effect is also manifested in the direction of the linkage isomerization observed for the 4-methylimidazole complexes; thus, it is found that the R form is the thermodynamically favored product. The values of $\Delta H°$ and $\Delta S°$ found for the acid dissociation constants of R and Ad (eq 3) may be compared to the values for imidazole forming imidazolate ($\Delta H° = 17.6 \pm 1.6$ kcal/mol, $\Delta S° = -7 \pm 5$ eu)[32] and the values for $(CN)_5Fe(Him)^{2-}$ ($\Delta H° = 8.8 \pm 0.8$ kcal/mol, $\Delta S° = -21 \pm 3$ eu).[33] The acid dissociation constants of R and Ad are within 1 kcal for $\Delta H°$ of the free ligand imidazole, suggesting an approximate cancellation of the withdrawing effect of Co(III) and the releasing effect of methyl on the ring. The more favorable $\Delta S°$ for the dissociation of R and Ad vs. the neutral imidazole and anionic $(CN)_5Fe(imH)^{2-}$ complex would be anticipated on the basis of reducing positive charge on the Co(III) complex, separating opposite charges for the neutral organic molecule, and increasing charge separation for the anionic Fe(III) system. The solvation appears to be slightly different for the R, R_{-H} and Ad, Ad_{-H} pairs as shown by the 10-eu larger $\Delta S°$ for dissociation of Ad, that is to say, a greater difference in solvation accompanies the deprotonation of Ad than for R. It seems logical for a pictorial view of the R and Ad isomers that the methyl group of R would perturb the solvation cage more than for the Ad isomer in the vicinity of the pyrrole hydrogen. A larger percentage change in solvation may then occur for the deprotonation of the Ad isomer upon establishing a strong H bond to the imidazolate anion, which is diminished if methyl perturbs the region.

A net lower free energy would exist for forming isomer R at the expense of Ad. That one is able to prepare isomer Ad must then be related to the kinetically slow linkage isomerization relative to the kinetic split between trapping either the R or the Ad orientation of 4-methylimidazole during the substitution process. R is the major product of the synthetic conditions. The entering ligand displaces Me_2SO in the synthetic procedure. The orientation and the degree of solvation of the entering ligand or the products are likely to be quite different in Me_2SO vs. those in H_2O, allowing formation of some Ad. It might also be mentioned that Toma[30] has concluded that histidine first coordinates to $(CN)_5Fe^{3-}$ in the hindered fashion, followed by rearrangement to the unstrained N. The isomerization at the $(CN)_5Fe^{3-}$ center is much more rapid than for $(NH_3)_5Co^{3+}$, which is entirely consistent with stronger Co^{III}–N bonds relative to Fe^{II}–N bonds and the magnitudes of the ligand field $10Dq$ values of related complexes.

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Registry No. V·3Cl⁻ (A = NH_3), 86568-75-4; VI·3Cl⁻ (A = NH_3), 86568-74-3; $(NH_3)_5Co(4\text{-methylimidazolate})^{2+}\cdot 2Cl^-$ (adjacent), 86568-76-5; $(NH_3)_5Co(4\text{-methylimidazolate})^{2+}\cdot 2Cl^-$ (remote), 86568-77-6; 4-methylimidazole, 822-36-6; $(NH_3)_5Co(imidazole)^{3+}\cdot 3Cl^-$, 86630-87-7; $(NH_3)_5Co(2\text{-methylimidazole})^{3+}\cdot 3Cl^-$, 86568-78-7.

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(34) (a) Mott, G. Ph.D. Thesis, University of Waterloo, 1980. (b) We have independently prepared the 3-picoline and 4-picoline complexes of $(NH_3)_5Co^{3+}$; the CH_3 groups are shifted diamagnetically and the α protons are shifted paramagnetically as described herein for the Ad and R isomers of 4-methylimidazole.
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Beryllium Nitrogen Compounds. 1. Monomeric Bis(amido)beryllium Compounds

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Monomeric beryllium amides of type $Be(NR_2)_2$ were prepared, in part, by a new method. Bulky R groups prevent oligomerization. Bis(diisopropylamido)beryllium dimerizes slowly and also adds pyridine. Dicoordination of beryllium results in a high-frequency shift of the ^9Be NMR signal and a rather large line width relative to tricoordinate Be.

Introduction

Among the amides of group 2A, those of the element beryllium are comparatively well characterized.[1] However, their chemistry is virtually unexplored. Four types of compounds are known, represented by the general formulas $Be(NR_2)_2$, $Be(N{=}CR_2)_2$, $XBeNR_2$ (X = organyl, hydride, halide), and $Be(NH_2)_3^-$. With the exception of $Be[N(SiMe_3)_2]_2$,[2] all beryllium bis(dialkylamides) do not exist as monomers. They dimerize, trimerize, or form adducts with Lewis bases such as pyridine to achieve tetracoordination at the beryllium center. BeN π-bonding, possible in BeN compounds of di- and tricoordinate Be, is obviously weak, and this is supported by data

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