π-Bonded Intermediates in Linkage Isomerization Reactions of a Tetrazole Coordinated to Pentaamminecobalt(III): An ^{15}N NMR Study

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Using regiospecifically ^{15}N-labeled complexes, the N-1 (adjacent-Me) to N-2 (remote-Me) linkage isomerization reaction of (5-methyltetrazolato)pentaamminecobalt(III) has been shown to be intramolecular in Me_2SO and H_2O as solvents. The results exclude a ligand dissociation and reentry mechanism or rearrangement via a symmetrical η^5 intermediate; an η^2 π-bonded tetrazolato intermediate is suggested. A degenerate remote-Me to remote-Me rearrangement (N-2 to N-3) has also been identified through the labeling experiments and shown to be intramolecular also. It is slower (25-fold) than the N-1 to N-2 rearrangement, as might be anticipated because the Me interaction with the bound NH_3 groups is diminished in the remote configuration. The N-1 isomer of the uncharged tetrazole ligand is some 100-fold faster to rearrange than its deprotonated form, but ^{15}N experiments show that this rearrangement is also intramolecular and does not proceed via an η^5 π-bonded intermediate or through dissociation and reentry of the ligand. A degenerate (and 10-fold slower) N-2 to N-3 rearrangement has also been identified for the uncharged ligand complex. Degenerate N-1 to N-4 rearrangements were not competitive with the N-1 to N-2 processes for either the anionic or uncharged ligand complexes. The large upfield shifts for the ^{15}N signals and in particular the strong negative NOEs observed in the proton-decoupled spectra establish N_4 as the site of protonation for the N-1 and N-2 isomers; the tautomers involved have not been established previously. Faster rearrangement for the more weakly bound neutral ligand complexes is consistent with an essentially dissociative, although still intramolecular, rearrangement process.

Introduction

Linkage isomerization reactions have been extensively studied in our group for a decade and a half.[1-4] The primary interest has been in pentaamminecobalt(III) complexes of ambidentate[5,6] and alterdentate[7] ligands, in providing a variety of leaving and entering groups and different ground state conformations and in order to understand the rate-controlling processes in some detail. Most of these rearrangements have been shown to be intramolecular, and isotopic tracer studies have been a key element in this mechanistic work. Furthermore, since the reactions are often acid- or base-catalyzed, NMR studies to elucidate the site of protonation or deprotonation have been another important aspect.

The adjacent-to-remote-R rearrangement of substituted tetrazoles coordinated to cobalt(III) has been examined for a range of R groups,[8,9] and such a process for the 5-methyl derivative used in the present work is shown in Figure 1. The related rearrangement of the 4-methylimidazolato complex (Figure 2) has been investigated by Shepherd et al.,[10] and the corresponding 4-bromo derivative, by Blackman et al.[11] For the imidazolato ions, cobalt migration to the immediately adjacent center involves

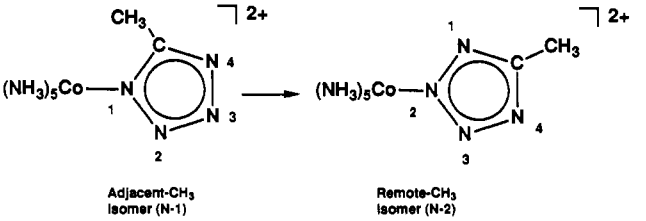

Figure 1. Adjacent- to remote-methyl (N-1 to N-2) rearrangement for (5-methyltetrazolato)pentaamminecobalt(III).

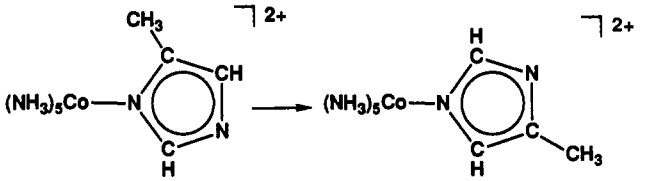

Figure 2. Adjacent- to remote-methyl (N-1 to N-4) rearrangement for (4-methylimidazolato)pentaamminecobalt(III).

formation of a C-bonded ylide, the possible formation of which en route to the remote substituent isomer has been eliminated.[10,11] Thus cobalt migrates directly across two ring atoms.

There are at least three facets of these rearrangements which merit further investigation. First, H^+ accelerates the rearrangement of coordinated tetrazolates but slows the corresponding imidazolato reaction.[8,10,12] This has been ascribed to the proton residing on the attacking nitrogen atom in the latter case, but the actual site of protonation in the complexes of tetrazoles has not been established. Second, the intramolecular nature of the process has not been proven. Last, a number of π-bonded intermediates (or transition states) have been suggested[10-12] for these rearrangements, but it was recognized that there was no definitive evidence for a particular species, if indeed any are involved. Some possibilities are shown in Figure 3 for the tetrazolato complex,

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(1) The results reported herein were presented at the 29th International Conference on Coordination Chemistry, Lausanne, Switzerland, July 1992 (see ref 14).

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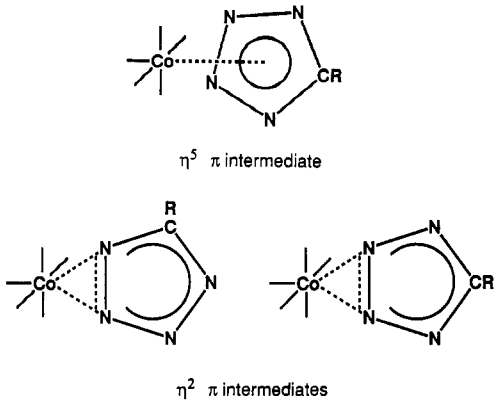


Figure 3. Possible π-bonded intermediates in the isomerization and isotopic scrambling reactions of (tetrazolato)cobalt(III) complexes.

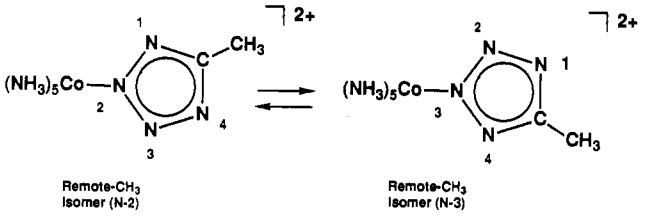


Figure 4. Remote- to remote-methyl (N-2 to N-3) rearrangement for (5-methyltetrazolato)pentaamminecobalt(III).

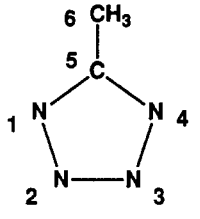
and there will be a similar set for the complexes of the uncharged tetrazole; of these, only the top one is a reasonable possibility for the substituted imidazolato species. The prospects of ligand dissociation (solvolysis) and reentry need also be considered, and this does not necessarily imply parallel *net* solvolysis. Recent careful work[13] showed that part of the classic Co–SCN to Co–NCS rearrangement occurs via NCS^- dissociation and reentry, albeit there is negligible net hydrolysis.

It will become apparent that the intramolecular process via simple η^2 π-bonded intermediates can be distinguished from other processes using ^{15}N NMR spectroscopy. This article describes the results of ^{15}N labeling and ^{15}N, ^1H, and ^{13}C NMR experiments[14] which permit these mechanistic distinctions and which allow unambiguous assignments for specific signals in the NMR spectra. We have also identified and studied the degenerate N-2 to N-3 rearrangement which amounts to an isotopic scrambling process ($N_2 \rightleftharpoons N_3$; $N_1 \rightleftharpoons N_4$; Figure 4).

We have performed similar work for the rearrangements of the uncharged tetrazole, the so-called acid-catalyzed rearrangements, in an attempt to identify unambiguously the site of protonation for both the N-1 and the N-2 tetrazolato complexes, since these results bear on the rearrangement mechanism.

Results and Discussion

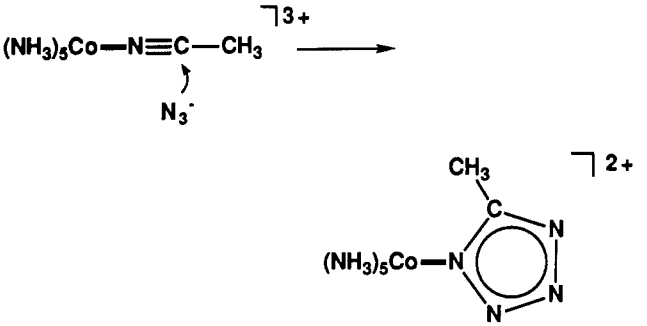
Throughout this paper, the nitrogen atoms in the tetrazole ring have been labeled with anticlockwise numbering:



Such a convention[15] is important since the symmetry is removed when cobalt is attached. The symbolism N-1, N-2, N-3, or N-4 has been used to refer to complexes bonded through the tetrazole nitrogen atoms N_1, N_2, N_3, or N_4, respectively. The N-1 and N-4 isomers are chemically identical and are referred to as the adjacent-methyl isomers,[10] but note that they are distinguished by NMR spectroscopy by introducing one or more ^{15}N labels in appropriate positions. Similarly, the more stable remote-methyl N-2 and N-3 isomers are identical, but can also be distinguished by ^{15}N incorporation.

Synthesis. We required regiospecifically labeled N-1 and N-2 methyltetrazole complexes with one and two labels at known positions; complexation removes the C_2 symmetry of the free ligand, so all four nitrogens are inequivalent in each isomer.

The unstable N-1 tetrazolato isomers are made by reacting coordinated nitrile with azide ion:[9]



The reaction is relatively rapid (complete in under 2 h at 20 °C in 1 M NaN_3),[16] certainly much more rapid than isomerization of the N-1 product to its N-2 linkage isomer.[9,12] At pH 8 the base-catalyzed hydration to the N-bonded amide[17] is not competitive, and we have found that keeping the pH low with acetate buffer[8,9] is not necessary. The corresponding stable N-2 isomers are made either by isomerizing the N-1 forms or by directly reacting a suitable precursor such as $[(NH_3)_5CoOH_2]^{3+}$ with the free tetrazolato anion and heating.[9,18,19]

The nature of the synthesis of the N-1 isomers lends itself to regiospecific labeling of the resultant tetrazole with ^{15}N. We have successfully prepared an N-1 tetrazolato complex labeled only at the bound nitrogen by using $[(NH_3)_5Co^{15}NCMe]^{3+}$ and unlabeled azide. This will be referred to simply as the nitrile-labeled complex. Also synthesized were an azide-labeled species (this is a 50:50 mixture of isotopomers—vide infra), from $[(NH_3)_5CoNCMe]^{3+}$ and terminally labeled azide $^{15}NNN^-$, and an azide–nitrile double-labeled species using ^{15}N in both the nitrile and azide (again, a 50:50 isotopomer mixture), all by essentially the same method.[20] The use of the less expensive $^{15}NNN^-$ instead of $N^{15}NN^-$ reduces the regiospecificity, but double-labeling allowed unambiguous assignments of the ^{15}N NMR signals.

A method was developed to maximize the yield of nitrile complex made from $^{15}NCMe$ (100% enriched). The product was spectroscopically identical to the known complex[21] except that the ^{13}C–^{15}N and $^1H(CH_3)$–^{15}N couplings were evident in the ^{13}C and ^1H NMR spectra, respectively (Table 1, supple-

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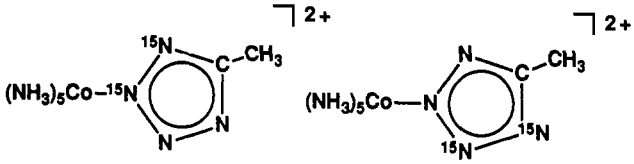
mentary material). For all the tetrazolato complexes, the ^1H and ^{13}C NMR spectra established the absence of any N-bonded amide, a possible impurity[9] and known[17] compound.

The ^{15}N-labeled N-2 isomers were not synthesized by the anation route[18,19] since this must involve scrambling. The unsymmetrically double-labeled ligand for example would yield a statistical mixture of the two species:



The labeled N-2 isomers were not isolated but were generated in situ from the N-1 forms simply by isomerization (Figure 1). Following this process, we identified the N-2 to N-3 rearrangement (Figure 4), which precluded isolation of *pure*, regiospecifically labeled N-2 isomers. It did however lead to the assignment of the N_1 and N_4 nitrogens of the N-2 isomer. Similarly, by use of ^{15}N in different positions in the N-1 reactant, all nitrogens in the N-2 species could be systematically and unambiguously identified by following the N-1 to N-2 to N-3 rearrangements for each reactant. Finally, we synthesized double-labeled N-1 and N-2 isomers from azide ion labeled both centrally and terminally, to identify N_3 for the N-1 complexes, to confirm their position for the N-2 complexes, and to provide additional ^{15}N–^{15}N coupling information.

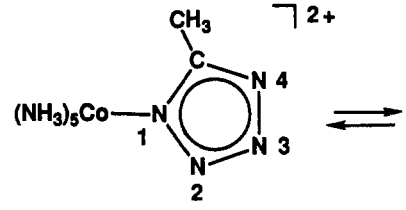
The N-1 and N-2 complexes of the neutral tetrazole were conveniently generated in situ in Me_2SO using a molar excess of CF_3SO_3H. In water, the pK_a's are 1.5 and 1.7, respectively,[10] and they seem to be comparably acidic in Me_2SO. By varying the amount of acid and observing the shifts in the ^1H, ^{13}C, and ^{15}N NMR spectra, we established the conditions for complete protonation. In Me_2SO, the protonated N-1 species is appreciably faster to rearrange than its deprotonated ion, as is the case[8,12] in water.

Characterization of Isotopically Labeled Tetrazolato Species. The N-1 and N-2 isomers for the 5-methyltetrazolato complex have been previously characterized by Purcell et al.[9,12] The ^1H and ^{13}C spectra are quite distinct (Table 1, supplementary material), and isomeric purity can be therefore clearly established. The ^{15}N NMR spectra are also quite different (vide infra). The ^1H and vis/UV spectra have been reported for both isomers previously,[9,18] but the ^{13}C NMR spectrum[18] and crystal structure[22,23] are known for only the N-2 form. There have been no ^{15}N studies for either of the methyltetrazole isomers but two such studies for the N-2 isomer of cyanotetrazole, one at natural abundance[24] and the other[18] for the general rather than regiospecifically ^{15}N-enriched species.

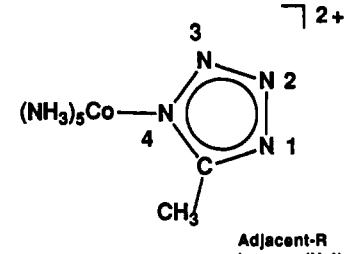
The ^{15}N-labeled acetonitrile complex shows a single sharp peak in water or Me_2SO; the sharpness is uncharacteristic of Co–N in general but probably reflects the linear Co—N≡C– arrangement. Contrast the N-1 tetrazole derived from this labeled nitrile complex and unlabeled azide which shows a singlet (N_1) that is somewhat broader, due no doubt to coupling to quadrupolar cobalt to which it is directly attached; this is a characteristic of Co–^{15}N in the ^{15}N NMR spectra for all the tetrazole species (Figure 5). [Curiously, the Co–^{15}N signal in the N-2 isomer is much broader (vide infra).] The retention of the Co–^{15}N bond in the synthesis is also apparent.

The ^{15}N NMR spectrum of the azide-labeled N-1 complex, synthesized from the unlabeled nitrile complex and $^{15}NNN^-$, shows the expected two additional peaks, of equal intensity due to the statistical distribution of the label between N_2 and N_4. In the spectrum of the azide- and nitrile-labeled complex (100% ^{15}N at N_1 and 50% ^{15}N at each of N_2 and N_4), the lowest field signal appears at the position seen in the previous spectrum but as a sharp doublet; the other signal from the previous spectrum remains a sharp singlet. These two signals are therefore N_2 (coupled to N_1) and N_4, respectively (Figure 5). The third, broader and double-intensity peak which appears at the expected position in the spectrum of the azide- and nitrile-labeled species is obviously N_1 although the expected doublet is not resolved. Thus for the N-1 isomer three of the four nitrogens were observed and assigned. The position of the remaining N_3 signal was determined from the ^{15}N NMR spectrum of the azide-double-labeled complex where, as expected, it appeared as a doublet at twice the intensity of the doublets for N_2 and N_4.

It was conceivable that the N-1 isomer could undergo a degenerate transformation such that, on isomerization, a label at N_1 could end up at N_4; this would require a 50:50 distribution at equilibrium and a two-line ^{15}N NMR spectrum. Also for such a rearrangement, the label at N_4 in the azide-only labeled species would migrate to N_1, and the label at N_2, to N_3, yielding a four-line NMR spectrum with two of these lines in common with the starting N-1 isomer spectrum. Furthermore, there would be no changes in the ^1H NMR spectrum corresponding to those changes in the ^{15}N NMR spectrum for such a process:



Adjacent-R isomer (N-1)



Adjacent-R isomer (N-4)

The ^{15}N NMR spectrum of the material initially derived from solution isomerization of the nitrile-only labeled N-1 isomer shows one line while the product obtained from isomerization of the azide-only labeled N-1 isomer shows two new lines (Figure 6, supplementary material). The product must therefore be the N-2 rather than N-4 species, confirmed by the concomitant changes in the ^1H NMR spectrum. These three new lines must therefore be the three nitrogens N_1, N_2, and N_4 of the N-2 isomer. Clearly, the degenerate adjacent-Me to adjacent-Me isomer rearrangement (N-1 to N-4) is not competitive with this adjacent-Me to remote-Me isomerization (N-1 to N-2).

The individual nitrogens of the N-2 isomer were also assigned using the spectra for the double labeled (azide and nitrile) species and the two monolabeled (nitrile-labeled and azide-labeled) complexes (Figure 6, supplementary material); the first showed a sharp triplet for N_1, a broad singlet (unresolved doublet, of half the intensity), clearly attributable to the metal ion bound N_2, and a sharp singlet for N_4 (also of half intensity, and too remote from the other label to be detectably coupled). This N_1 triplet actually

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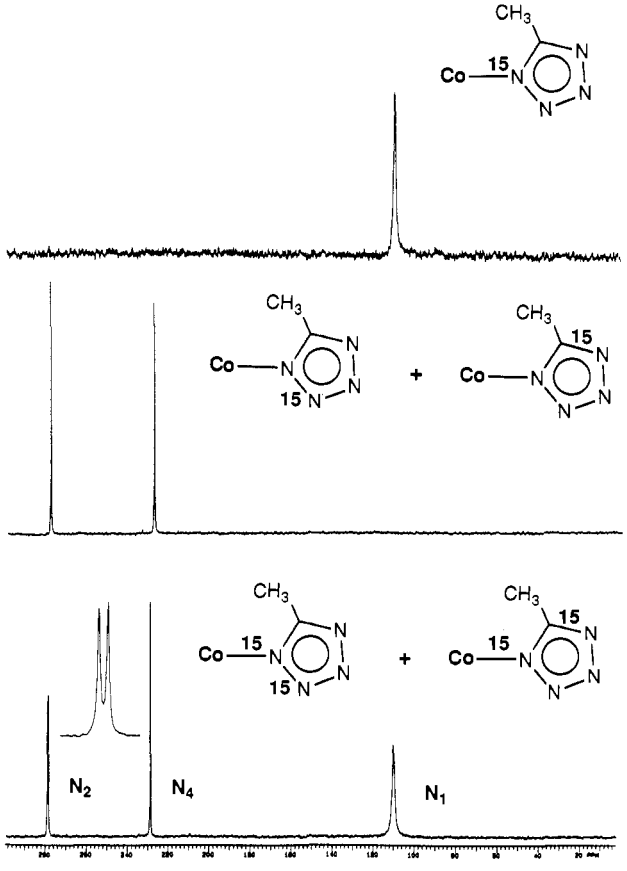

Figure 5. ^{15}N NMR spectra for several enriched N-1 bonded (5-methyltetrazolato)pentaamminecobalt(III) ions in Me_2SO-d_6: top, nitrile-labeled species; middle, azide-labeled species; bottom, azide–nitrile double-labeled species. The inset in the bottom spectrum shows the lowest field doublet expanded.

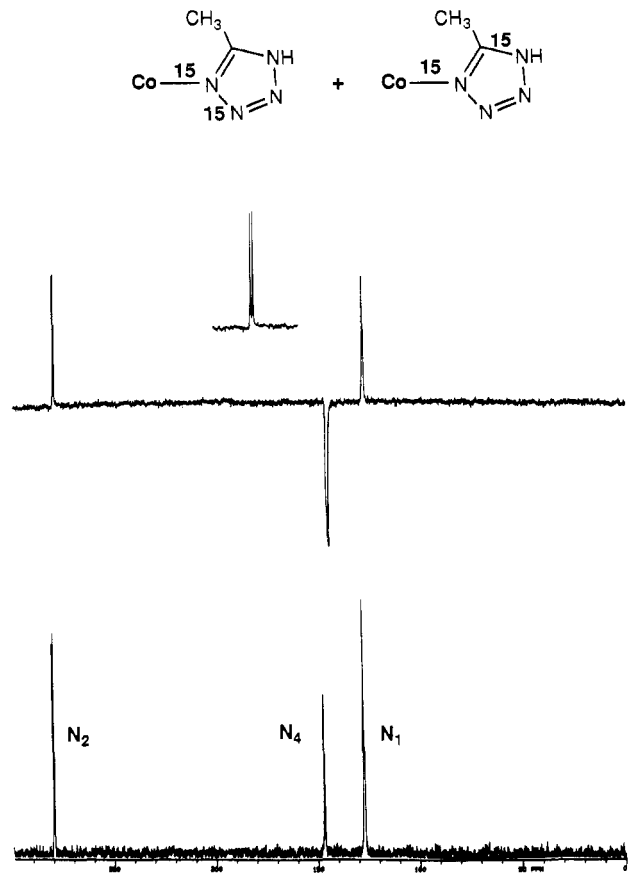

Figure 7. ^{15}N NMR spectra for the azide–nitrile double-labeled N-1 bonded (5-methyltetrazole)pentaamminecobalt(III) ion in Me_2SO-d_6: upper, ^1H-decoupled spectrum showing the strong negative NOE for the N_4 nitrogen attached to the proton; lower, ^1H-coupled spectrum, showing N–N coupling in both N_2 and the cobalt bound nitrogen N_1. The inset in the upper spectrum shows the lowest field doublet expanded.

comprises a central singlet due to the ^{15}N at N_1 flanked by two ^{14}N nuclei, superimposed on an off-centered doublet due to the two adjacent ^{15}N species (see inset, Figure 6, supplementary material). The small but clear off-centering (ca. 3 Hz upfield) reflects an isotopic shift due to α substitution of an ^{14}N by an ^{15}N and was observed in a number of similar species (see insets in Figure 8, supplementary material, for example).

The remaining ^{15}N signal, that for the unlabeled atom N_3, was located through the isotopic scrambling process of the azide-labeled complex (N-2 ⇄ N-3) which interchanged labeled N_2 with unlabeled N_3 (vide infra). The result was confirmed by a direct recording of the ^{15}N NMR spectrum of the N-2 isomer of the azide-double-labeled complex, for which the double-intensity doublet must be the N_3 signal.

Characterization of the ^{15}N-Labeled Tetrazole Complexes. For the study of the protonated species, ^{15}N NMR spectra were recorded using only double-labeled complexes, mostly the azide- and nitrile-labeled species but also the azide-double-labeled complex. In the ^1H-coupled spectra for the azide- and nitrile-labeled species (lower spectra, Figures 7 and 8; Figure 8 is supplementary material), assignments were clear because the N_1 resonance was always twice as intense and the signal due to coordinated nitrogen was always broader than the other signals. These Co–^{15}N signals were much sharper than those of their corresponding deprotonated ions, and indeed the one-bond ^{15}N–^{15}N coupling is clearly observed for N_1 in the N-1 form and for N_2 in the N-2 isomer. Further, weak ^{15}N–^{15}N two-bond coupling was detected in the N-1 isomer for the species bearing two ^{15}N labels adjacent to the ring carbon, as seen in a doublet for N_4 ($J \approx 5$ Hz) but not for its broader N_1 partner. This was the only example of two-bond ^{15}N–^{15}N coupling observed for any of the ^{15}N NMR spectra reported herein.

The assignments for N_1, N_2, and N_4 in the N-1 isomer and all four nitrogens in the N-2 form each followed from the line of reasoning given for the corresponding tetrazolato species. The ^{15}N NMR spectra of the azide-double-labeled complexes proved the position of N_3 for the N-1 isomer and confirmed the assignments for the N_2 and N_4 signals. These particular spectra were also necessary to see the behavior of the N_3 signals on protonation.

The ^{15}N spectra were first recorded without broad-band decoupling; ^{15}N–^1H coupling was not detected, presumably because of the rapid proton-exchange rates in these very acidic complexes. However, the proton-decoupled ^{15}N spectra were quite informative (upper spectra, Figures 7 and 8). For each of the N-1 and N-2 isomers, one peak was inverted and dramatically increased in intensity. This is the nitrogen to which the proton is attached, N_4 in both cases. The signal inversion is quite characteristic of the ^{15}N nucleus which has a negative gyromagnetic ratio.[24] None of the other nitrogen centers, the N_3 site being of particular interest, showed any significant intensity differences between the proton-coupled and -decoupled spectra, and we conclude that the population of other tautomers, arising from alternative protonation sites, is negligible. This conclusion is supported in the analysis of the shift data reported below.

The ^{15}N signal assignments and ^{15}N–^{15}N coupling constants for the N-1 and N-2 tetrazolato and tetrazole complexes are summarized in Figure 9 (supplementary material); a complete listing of shifts and coupling constants is given in Table 1 (supplementary material).

^1H and ^{13}C NMR Spectra. Only the nitrile complex revealed ^1H–^{15}N coupling ($J = 3$ Hz) in the ^1H NMR spectra, a three-bond interaction (Table 1, supplementary material). In the ^{13}C

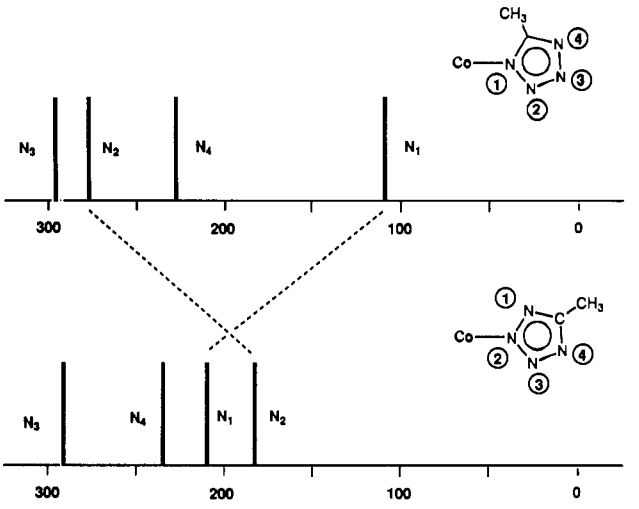

Figure 10. ^{15}N NMR chemical shifts (ppm) illustrating the strong shifts on going from the N-1- to N-2-bonded tetrazolato complex, upfield for N_2 on coordination and downfield for N_1 on decoordination.

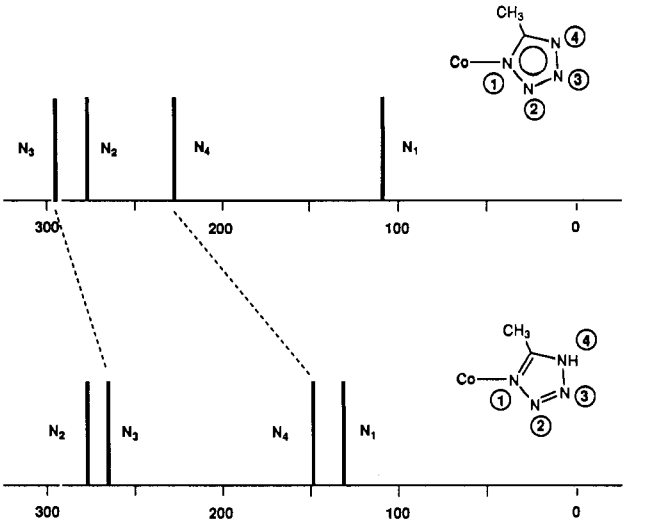

Figure 12. ^{15}N NMR chemical shifts (ppm) for the N-1-bonded isomer and its protonated form, illustrating the strong upfield shift for N_4 when a proton is attached, with little change in the other signal positions.

spectra, the nitrile complex showed ^{15}N coupling to only the α carbon (J_α = 36, J_β < 2 Hz) which compares with 17.5 and 3 Hz for α and β couplings in the free nitrile.[24] For the tetrazole complexes, only an ^{15}N adjacent to the sp^2 ring carbon produced a detectable ^{15}N–^{13}C one-bond coupling (ca. 3 Hz, whether in an N-1 or an N-2 isomer). The ^{15}N–^{13}C coupling to the more remote sp^3 methyl carbon is greater, ca. 5–8 Hz, across two bonds (Table 1, supplementary material).

In the ^{13}C NMR spectra, isotopic shifts were also observed in a number of species and were of the same order as found in the ^{15}N NMR spectra, ca. 3 Hz upfield, for α substitution of ^{14}N by ^{15}N.

The ^1H and ^{13}C NMR spectra for the N-1 and N-2 complexes of uncharged tetrazole, which are unremarkable, have not been reported previously. They are different from those of the tetrazolato ions, but not greatly, and certainly in no way characteristic of the site of protonation. Our ^1H NMR spectrum for the deprotonated N-1 isomer is somewhat different from that first reported[9] which more closely corresponds to our spectrum for the protonated form. It is probable that the early difficulties of cocrystallizing perchlorate salts for protonated and deprotonated N-1 isomers are responsible for the discrepancy; indeed, we had difficulty crystallizing the protonated N-1 isomer as a perchlorate. Also, we could not crystallize what we expected to be a less soluble 1:1 double salt, analogous to others we have discovered.[25-27] The protonated form of the N-2 isomer was, nonetheless, readily crystallized.

^{15}N NMR–Structure Correlations. The stick diagrams (Figures 10–13; Figures 11 and 13 are supplementary material) show the chemical shift relationships between the N-1 and N-2 tetrazolato (Figure 10) and tetrazole (Figure 11) isomers and between deprotonated and protonated forms for the N-1 (Figure 12) and N-2 (Figure 13) species.

The N_1 and N_2 signals in each of all four complexes differ not only because one is adjacent to carbon and one is not but also because cobalt(III) coordination results in a substantial upfield shift for the bound N resonance. Thus on going from an N-1 to N-2 isomer, the N_1 signal moves downfield while that of N_2 moves upfield, and they actually cross (Figures 10, 11). Second, on protonation, only the N_4 signal moves appreciably, upfield, for both the N-1 and N-2 isomers (Figures 12, 13). The magnitude and direction of the shift are consistent with exclusive protonation at this N_4 atom in each isomer, the nitrogen adjacent to C but further from the Co(III) center. This conclusion is consistent with the NOE observations discussed earlier. The N_3 signal is also moved upfield on protonation at N_4, but much less so, although enough in the case of the N-1 isomer to reverse the order of N_2 and N_3 signals compared to that of the parent tetrazolato ion. The sense and magnitude of the shift are not unexpected for an atom adjacent to the site of protonation, and we exclude an alternative explanation, namely some population of the tautomer having the proton directly attached to N_3, because no NOE was observed for this center in either the N-1 or the N-2 isomer.

Our assignments for the N-2 isomer of 5-methyltetrazole may be compared with two independent sets of data published for the corresponding N-2 isomer of 5-cyanotetrazolate in the same solvent.[18,24] Recognizing the different ligand numbering conventions used, and opposite chemical shift scales, the two studies are in remarkable agreement on chemical shifts, but the nitrogen assignments differ. In the natural abundance study,[24] the tetrazole nitrogens numbered by the present convention are, from high to low field, N_2, N_1, N_4, and N_3, in agreement with our assignments for the corresponding 5-methyltetrazolato complex. However, in the study employing the tetrazole-nitrogen-enriched ligand (general labeled),[18] the N_1 and N_4 assignments have been reversed.

N-1 to N-2 Rearrangements. We initially examined the tetrazolato complex rearrangements in D_2O but quickly discovered superior resolution of the ^{15}N signals in Me_2SO. It is clear from the ^{15}N NMR discussion above that the N-1 tetrazolato complex first isomerizes to an N-2 species having the same number of signals. This observation excludes a mechanism involving dissociation of the ligand and excludes formation of a symmetrical η^5 π-bonded intermediate (Figure 3). Both these possibilities require scrambling of the label between N_1 and N_4, as well as N_2 and N_3, and hence a simultaneous doubling in the number of signals. A mechanism involving the η^2 intermediate (Figure 3) seems reasonable and is not inconsistent with the facts, but other possibilities will always exist.

A similar set of experiments were performed on the azide- and nitrile-labeled N-1 tetrazole complex, with the same result—no scrambling of ^{15}N label. This reaction must therefore proceed intramolecularly, via an η^2 π-bonded intermediate similar to that generated by the tetrazolate, except for the addition of a proton. The rearrangement has a $t_{1/2}$ of ca. 3 h at ambient temperature and is thus some 50-fold faster than that for the tetrazolato complex ($t_{1/2}$ = ca. 6 days, 25 °C). This rate difference is similar to that observed[12] for water as solvent.

Under the conditions of the rearrangement in acid, the free ligand would be uncharged and therefore much less likely to

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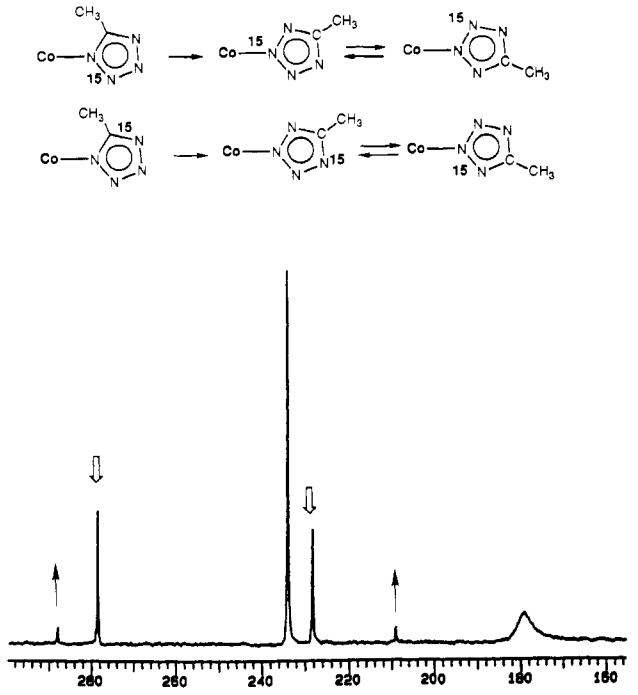

Figure 14. ^{15}N NMR spectra, at a particular time in the sequence of rearrangements, showing the N-1 to N-2 isomerization of the tetrazolato complex nearing completion (downward arrows identify the reactant N-1 isomer), while the reversible N-2 to N-3 isotopic scrambling process has just begun (upward arrows identify the N-3 isomer, showing the new resonance for N_2 which actually corresponds to position N_3 in the N-2 isomer).

reenter if dissociated. The lack of competing solvolysis is therefore consistent with intramolecular rearrangement, although of itself inconclusive.

N-2 to N-3 Rearrangements. The N-2 isomers over a long time give rise to new signals (Figure 14), and these signals correspond to scrambling of the label between N_1, N_4 and N_2, N_3; this reaction must ultimately occur because the constant for the equilibrium between the N-2 and N-3 species is unity. The simplest mechanism for this rearrangement is another migration of the cobalt, from N_2 to N_3, via an intermediate similar to that for the N-1 to N-2 rearrangement (Figure 3). These results in themselves do not exclude a simple ligand dissociation and reentry which could also effect the label scrambling. However it seems unlikely that the ligand is dissociated from the N-2 isomer but not, as we have shown, from the N-1, especially as the N-1 to N-2 and N-2 to N-3 rearrangement rates are not vasty different (vide infra). The proof that the isotopic scrambling process is intramolecular arose from an experiment in which some free ligand (molar excess) was added and the N-2 to N-3 rearrangement for the labeled complex was followed by ^{15}N NMR spectroscopy as before. No isotopic dilution was detectable, thereby excluding a ligand dissociation mechanism; the rearrangement must be intramolecular.

The relative rate for the consecutive processes N-1 to N-2 to N-3 is, in principle, defined from a single measurement in time when individual (relative) concentrations can be determined, such as from an ^{15}N NMR spectrum recorded at a particular reaction time; the time need not be known. Such a determination assumes the rate law and reaction scheme and requires the reaction to have proceeded to a point where all three species may be estimated with reasonable accuracy. The test of such an analysis is the consistency of the k_2/k_1 values obtained for different reaction times (k_1 and k_2 are the first-order rate constants for the N-1 to N-2 and the N-2 to N-3 processes, respectively).

The relationship among κ (the relative rate k_2/k_1), α (the fraction of residual N-1 isomer), and β (the fraction of accumulated N-2 isomer; α and β are fractions relative to total N-1 + N-2 + N-3) is readily derived along the lines of the standard treatment:[28]

$$\alpha^{\kappa} - (\alpha + \beta) + \beta\kappa = 0$$

Here $\kappa \neq 0$, and this equation can be solved readily using, e.g., Mathematica. The results so obtained for the present systems were $\kappa = 0.08$ for the deprotonated ions and 0.2 for the protonated species; in both cases the second step is slower. We note that k_2 in these systems is the rate constant for the sum of forward and reverse reactions, which for the second step, an isotopic scrambling process, are equal. Thus the actual relative rates for the conversions N-1 to N-2 and N-2 to N-3 are half the above values, 0.04 and 0.1, respectively, indicating slower second steps by factors of 25 and 10, respectively.

The rate reduction is accommodated by the reduced steric interaction[9] between the Me group and bound NH_3 ligand in the "remote" to "remote" rearrangement, as opposed to the "adjacent" to "remote" rearrangement. Indeed, it is the latter which is responsible for the remote-Me isomer being the significantly more stable species (by at least 8 kJ mol^{-1}); a significant component of this energy difference seems to be translated into the activation energy for the rearrangements since a factor of 10–25 corresponds to a 6–8 kJ mol^{-1} difference in activation energy.

The rearrangement for the deprotonated ions has been shown to be intramolecular, while for the uncharged ligand species a ligand dissociation and reentry route in acid can be excluded by the same argument advanced for the N-1 to N-2 process. No solvolysis is observed on the time scale of the N-2 to N-3 rearrangements for either the deprotonated or protonated species, as for the somewhat faster N-1 to N-2 rearrangements, consistent with intramolecular reaction pathways.

Comparison with Recent ^{15}N Work. The present results were first communicated[14] in mid-1992. However, following submission of the present work, we became aware of a paper submitted by Hubinger et al. in Feb 1993 (published May 1993[29]) which did not recognize this and where there had been some overlap. They reported the preparation of an ^{15}N-labeled N-1 isomer (our "azide-only" labeled material) and its rearrangement to the N-2 and then the N-3 isomer, with conclusions similar to ours. The present work deals with this and related chemistry in greater depth. Furthermore, we have studied the ^{15}N NMR spectra and rearrangements of the more reactive protonated 5-methyltetrazole species, and unambiguously assigned the tautomers. The comparison of the ^{15}N NMR spectra with the corresponding spectra for the deprotonated ions has been particularly informative. For both the tetrazole and tetrazolato complexes, we have quantified the relative rates for the various possible rearrangements, shown that the N-2 to N-3 rearrangement is intramolecular, considered the prospects of a degenerative N-1 to N-1 rearrangement, and unambiguously assigned all the ^{15}N signals using azide-only, and nitrile–azide, and azide double-labeled species, in addition to the nitrile-only labeled species. Hubinger et al.[29] tentatively assigned some signals for the tetrazolato ions by comparison with free ligand; their assignments nonetheless are the same as ours. They reversed their earlier[18] assignments for the N_1 and N_4 nitrogens of the N-2 cyanotetrazolato species, and these are now in agreement with our assignments for the same species and with those published earlier by others.[24]

Summary and Conclusions

The N-1 bonded tetrazole complex isomerizes to its more stable N-2 isomer intramolecularly. Observed through ^{15}N scrambling, the cobalt then proceeds to migrate to the next adjacent nitrogen in the ring, also intramolecularly. Both these reactions are

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appreciably acid-catalyzed, and the ligand never leaves the metal ion. The acceleration in acid is inconsistent with the "tight ion-pair" mechanism, one of several proposals for intramolecular rearrangements of this kind,[5] since one component is neutral. The flat η^5 π-bonded intermediate (Figure 3) and a ligand dissociation and reentry mechanism are also eliminated by the ^{15}N experiments.

The reactions are base-catalyzed (which is usual), but only mildly so,[12] and thus ^{15}N experiments for these reactions were not pursued because of the tendency to decompose in strong base. We note that while the *reaction* is base-catalyzed,[12] it has never been established that it is the linkage isomerization process which is actually base-catalyzed, since the base dependence of the product distribution (N-2 tetrazolato and hydroxo species) does not appear to have been examined.

The site of protonation for both the N-1 and N-2 isomers has been established; it is exclusively the N_4 atom in both cases. Since this is not the incoming nitrogen for the N-1 isomer rearranging to the N-2 form, acid accelerates rather than slows the process; a neutral leaving group is superior to an anionic one in dissociative substitution reactions of octahedral cobalt(III) complexes. The effect of acid should be contrasted with the corresponding process for 4-methylimidazole,[10] where acid resides on the incoming nitrogen and the process is slowed, despite the neutral leaving group. There is no other readily accessible tautomer for the imidazole complex, and quite likely therefore the ligand may be dissociated and the other site protonated before reentry. This possibility remains to be tested.

The prospect that the N-1 form could be regenerated (through isomerization to the N-4 complex) competitively with isomerization to the N-2 isomer was also examined using ^{15}N NMR spectroscopy. However, such a degenerative N-1 to N-4 rearrangement was found not to be competitive. This fact in itself indicates that ligand dissociation and reentry do not occur.

The relief of steric congestion between the coordinated NH_3 and the adjacent-Me group in the N-1 isomer has been advanced as the reason for the superior stability of the N-2 isomer.[12] The new observation of slower remote-Me to remote-Me isomerization reactions, through the use of an ^{15}N tag and observation of isotopic scrambling, provides some evidence for this suggestion, since the process is devoid of this interaction for both the protonated and deprotonated species.

Experimental Section

NMR spectra were recorded on a Varian XL300 spectrometer using a 5-mm broad-band probe (20 °C) tuned to 75.48 MHz for ^{13}C and 20.28 MHz for ^{15}N. Shifts are reported as ppm downfield from $SiMe_4$ (^1H, ^{13}C; Me_2SO-d_6) or $NaNN^{15}N$ (^{15}N, Me_2SO or D_2O); ^{15}N shifts relative to external $MeNO_2$ are obtained by subtracting 279 ppm. For the ^{15}N spectra of the tetrazole complexes in Me_2SO containing excess acid (CF_3SO_3H), NaN_3 reference was omitted and the spectra were run with the previous machine settings for referencing to NaN_3. Acquisition parameters were standard except for those of the ^{15}N NMR spectra where a 90° pulse and a total repetition time of 20 s were employed. Relaxation agents were deliberately avoided so peak heights could be more easily related to ^{15}N enrichments. The decoupler was turned off except in a set of experiments that were performed on the complexes of the uncharged tetrazole ligand designed to see the NOE and where standard broad-band decoupling was used. Visible and UV spectra were recorded on an HP8452A diode array or a GBC918 spectrophotometer. Labeled azide ($NaNN^{15}N$, 100 atom %) and [^{15}N]acetonitrile (100 atom %) were purchased from Cambridge Isotope Laboratories. A sample of ^{15}N-enriched NaN_3, which was believed to be $Na^{15}NNN$ but which fortunately was found to contain both $NaN^{15}NN$ (35%) and $Na^{15}N^{15}NN$ (35%), was a gift from Professor A. M. Sargeson. 5-Methyltetrazole[30] was synthesized as described on a small scale, while other chemicals were AnalaR grade or an equivalent.

The starting nitrile complex was made by the standard triflate method[21] using neat acetonitrile as solvent and isolated as the triflate salt. A modified method was also developed which was more economical regarding the nitrile, so that it could be used for the ^{15}N-labeled material. Acetone and sulfolane were tried as diluting solvents, with acetone superior for the purpose. Complexes purified for characterization purposes by recrystallization had the published[21,31,32] vis/UV and ^1H and ^{13}C NMR spectra.

The N_1-bonded complex $[(NH_3)_5Co(CH_3N_4)](CF_3SO_3)_2$ was prepared essentially as described,[20] by dissolving $[(NH_3)_5CoNCCH_3](CF_3SO_3)_3$ in 1 M NaN_3 at ambient temperature until saturated, filtering, and allowing to stand overnight. Buffering with acetic acid/acetate was found to be unnecessary. On cooling, the product was filtered off, washed with 2-propanol and ether, and air-dried. It could be recrystallized from a saturated solution in 0.01 M Tris using concentrated aqueous $NaCF_3SO_3$ as the precipitant or converted to the perchlorate by two recrystallizations using $NaClO_4$ instead of $NaCF_3SO_3$. Tris was employed to avoid the problem of cocrystallization of the protonated form reported by Ellis and Purcell.[9] The NMR spectra (^1H, ^{13}C, ^{15}N) established purity, together with satisfactory elemental analyses and internally consistent molar extinction coefficient data for the different salts (ϵ_{476} 63.0, ϵ_{342} 57.5; 0.01 M Tris in H_2O; lit.[9] ϵ_{473} 62.0, ϵ_{335} 77; H_2O).

The N-2 isomer was synthesized from the N-1 form by allowing a saturated solution in water to isomerize over a period of 2 weeks. Alternatively, the isomerization was carried out in 0.1 M triflic acid overnight, and the product solution was neutralized to pH 8 with NaOH (0.95 equiv) and Tris before crystallization. The product was recrystallized as described for the N-1 form above. The protonated N-2 isomer was obtained from a saturated solution of the deprotonated form in water (triflate salt) by addition of one-quarter volume of $HClO_4$ (70%). After cooling, it was filtered off, washed copiously with ether, and air dried. It was characterized by its vis/UV spectrum in 0.01 M Tris, giving the correct formula weight for the triperchlorate monohydrate. The NMR spectra indicated stoichiometric and isomeric purity, and elemental analyses were satisfactory. Vis/UV spectra: ϵ_{466} 65.0, ϵ_{336} 69.5; 0.01 M Tris in H_2O; lit.[9] ϵ_{465} 64, ϵ_{342} 86; lit.[18] ϵ_{464} 64.8, ϵ_{334} 65.5; H_2O.

The ^{15}N-labeled N-1 compounds were made by precisely the above methods but on a small scale (ca. 0.2 g of nitrile complex, labeled or unlabeled, in 1 M normal NaN_3, $NaNN^{15}N$, or $NaN^{15}N^{15}N$). [Excess $Na^{15}N_3$ was obtained from the filtrates by dilution, sorption, and elution (H_2O) from SP Sephadex C-25 (Na^+ form), followed by freeze drying.] For the labeled-nitrile complex, 1.0 g of triflato triflate complex in acetone containing 1.1 equiv of $[^{15}N]CH_3CN$ was used. The ^1H and ^{13}C NMR spectra of this product were identical to those of the unlabeled material except for the clear ^{13}C–^{15}N and $^1H(CH_3)$–^{15}N couplings (Table 1, supplementary material).

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Supplementary Material Available: Table 1 (^1H, ^{13}C, and ^{15}N NMR data for labeled acetonitrile and 5-methyltetrazole complexes of pentaamminecobalt(III)), Figures 6 and 8 (^{15}N NMR spectra), and Figures 9, 11, and 13 (^{15}N spectral data) (11 pages). Ordering information is given on any current masthead page.

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