

# Nitrogen-15 NMR Studies of Tetrazole Complexes of Pentaamminecobalt(III). Implications Concerning the Transition State for Linkage Isomerization

S. Hubinger, J. H. Hall, and W. L. Purcell\*

Department of Chemistry, University of Miami, Coral Gables, Florida 33124, and Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received February 11, 1993

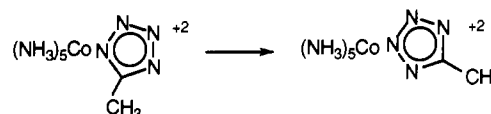
Synthesis of the N1-bonded (5-methyltetrazolato)pentaamminecobalt(III) complex utilizing sodium azide enriched in  $^{15}\text{N}$  at the terminal nitrogen has produced a complex enriched specifically at the N2 and N4 ring positions. This has permitted the assignment of all four nitrogen signals in the natural-abundance  $^{15}\text{N}$  NMR spectrum of the complex. A similar natural-abundance NMR spectrum for a novel chelated amidine complex which is also N1 bonded is reported along with its synthesis and purification. Following the  $^{15}\text{N}$  NMR of the linkage isomerization of the enriched complex in solution to the N2-bonded form has also permitted an  $\eta^5$  and certain  $\eta^3$  transition-state structures to be eliminated from consideration for the isomerization process. The data suggest an  $\eta^2$  transition state is utilized. A subsequent N2-to-N3 isomerization of the N2-bonded complex has also been discovered from the  $^{15}\text{N}$  NMR study. The enrichment study also indicates that previous assignments of ring nitrogen signals N1 and N4 in similar N2-bonded tetrazolato complexes of cobalt(III) may be in error.

## Introduction

The linkage isomerization of N1-bonded 5-substituted tetrazolate ligands bound to the pentaamminecobalt(III) moiety to their N2-bonded form, shown in Scheme I, was first reported in 1982<sup>1</sup> and has now been clearly established *via* kinetic studies.<sup>2–4</sup> Bonding *via* the N2 ring nitrogen in the final product has been firmly established for the (5-cyanotetrazolato)pentaamminecobalt(III) complex by both a single-crystal X-ray structure determination<sup>5</sup> and  $^{15}\text{N}$  NMR studies on specifically labeled ligands<sup>6</sup> which showed separate resonances for all four ring nitrogens as well as the nitrile nitrogen. These  $^{15}\text{N}$  NMR assignments have since been used for assigning N2 bonding in a number of other cobalt(III)–tetrazole complexes.<sup>7</sup> However, the N1-bonding mode has not been established by such direct methods. For N1-bound complexes, the method of synthesis, elemental analysis, and infrared spectra have established the presence of the tetrazole ring, and UV–visible and infrared spectral characterization have established that these complexes, while bonded to a nitrogen, are not identical to the N2-bonded complexes, thus, establishing N1 bonding as the only viable alternative assignment.<sup>1,8</sup> In this paper we report on the natural-abundance  $^{15}\text{N}$  NMR spectra of two N1-bonded (tetrazolato)pentaamminecobalt(III) complexes as well as the spectrum of an  $^{15}\text{N}$ -enriched, specifically  $^{15}\text{N}$ -labeled form which allows unambiguous peak assignments for the four ring nitrogens.

Similarly, little is known about the transition state employed for the N1-to-N2 linkage isomerization. Indeed, little is known about the transition states employed for most linkage isomerization processes. Although evidence for a  $\pi$ -bonded intermediate was given in 1982 for the extensively studied nitrito-to-nitro isomer-

## Scheme I



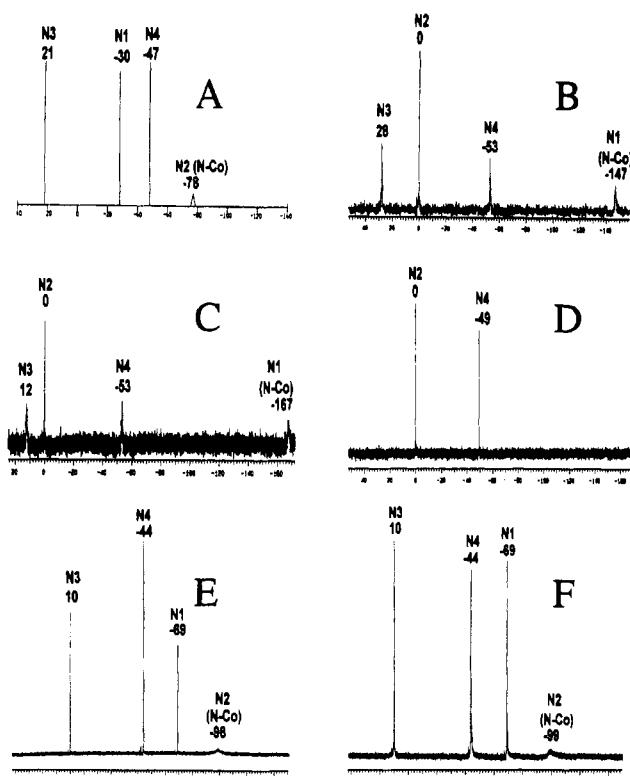
ization,<sup>9</sup> the isotope-labeling experiment central to the development of that conclusion now seems to be in dispute.<sup>10</sup> The availability of a synthetic route to a specifically labeled 5-methyltetrazolato complex has allowed us to examine certain aspects of the transition state for linkage isomerization which are also reported herein.

## Results

**Characterization of a Derivative of (5-Cyanotetrazolato)pentaamminecobalt(III).** Heating a dimethyl sulfoxide (DMSO) solution of N2-bonded (5-cyanotetrazolato)pentaamminecobalt(III) produces a new complex which has a  $\lambda_{\text{max}}$  at 473 nm in neutral and acidic solutions, consistent with N1 bonding of the tetrazolato ring.<sup>1,6,11</sup> However, in basic medium the peak maximum undergoes a red shift to 478 nm which is not observed with other tetrazolato complexes prepared to date. The infrared spectrum of the bromide salt of this derivative has peaks in the 1000–1200-cm<sup>-1</sup> region consistent with the tetrazolato ring system,<sup>1,6,11</sup> while the characteristic 2260-cm<sup>-1</sup> cyanide stretching frequency of the starting material is absent. There is also a sharp, medium intensity peak at 1250 cm<sup>-1</sup> which is found in N1-bonded tetrazolato complexes but is absent in their N2-bonded analogs.<sup>1</sup> The proton NMR spectrum of this complex (*versus* TMS in DMSO-*d*<sub>6</sub>) is more complex than that of the starting material, with resonances at 3.06, 3.73, 3.92, 6.69, and 8.55 ppm. Overlap of the broad signals at 3.73 and 3.92 ppm precludes separate integration of the five signals observed for this complex. However, the 3.06 ppm signal does integrate at nearly 1:1 to the total integrated value of these two resonances (1:0.92). The 8.55 ppm signal area is approximately twice that of the 6.69 ppm resonance (1.89:1), and these latter two resonances disappear rather rapidly

- (1) Ellis, W. R.; Purcell, W. L. *Inorg. Chem.* **1982**, *21*, 834.
- (2) Purcell, W. L. *Inorg. Chem.* **1983**, *22*, 1205.
- (3) Hall, J. H.; Purcell, W. L. *Inorg. Chem.* **1990**, *29*, 3806.
- (4) Hubinger, S.; Purcell, W. L. *Inorg. Chem.* **1991**, *30*, 3707.
- (5) Graeber, E. J.; Morosin, B. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 567.
- (6) Balahura, R. J.; Purcell, W. L.; Victoriano, M. E.; Lieberman, M. L.; Loyola, V. M.; Fleming, W.; Fronabarger, J. W. *Inorg. Chem.* **1983**, *22*, 3602.
- (7) Nelson, J. H.; Takach, N. E.; Henry, R. A.; Moore, D. W.; Tolles, W. M.; Gray, G. A. *Magn. Reson. Chem.* **1986**, *24*, 984.
- (8) Lopez de la Vega, R.; Ellis, W. R.; Purcell, W. L. *Inorg. Chim. Acta* **1983**, *68*, 97.

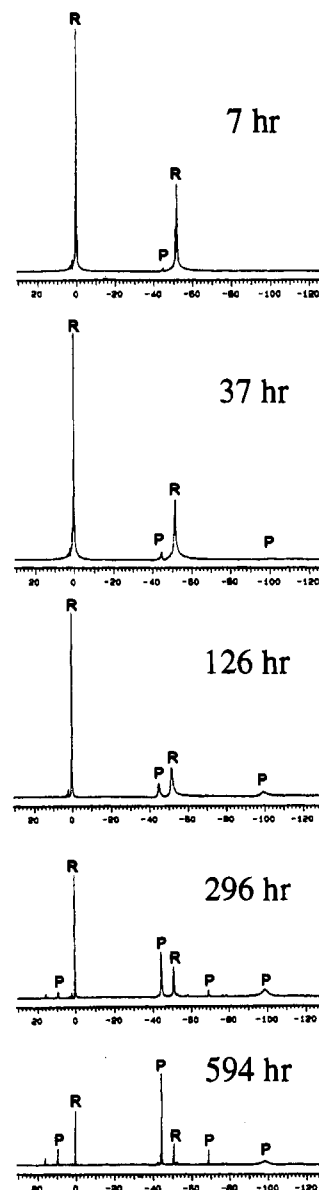
- (9) Jackson, W. G.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 70.
- (10) Jackson, W. G. *Inorg. Chim. Acta* **1988**, *149*, 101.
- (11) Hall, J. H.; Lopez de la Vega, R.; Purcell, W. L. *Inorg. Chim. Acta* **1985**, *102*, 157.



**Figure 1.**  $^{15}\text{N}$  NMR spectra of aminocobalt(III) tetrazolato complexes in the tetrazole ring nitrogen region. All chemical shifts are in ppm from an external nitromethane reference. All spectra were obtained in deuterated DMSO unless noted otherwise. (A) A representation of the spectrum of the ring nitrogens of the N2-bonded (5-cyanotetrazolato)-pentaamminecobalt(III) complex from ref 6. Note: We feel the N1 and N4 nitrogen signal assignments shown from ref 6 should be reversed (see text). Assignments of peaks in spectra B–F are described in the text. (B) Natural-abundance spectrum of the amidine chelate complex (I). (C) Natural-abundance spectrum of the N1-bonded (5-methyltetrazolato)-pentaamminecobalt(III) complex. (D) Spectrum of the N1-bonded 5-methyltetrazolato complex specifically enriched in  $^{15}\text{N}$  at positions N2 and N4. (E) Spectrum of the enriched complex for D after 6 linkage isomerization half-lives in DMSO. (F) Spectrum of the enriched complex for spectrum D after 6 linkage isomerization half-lives in water.

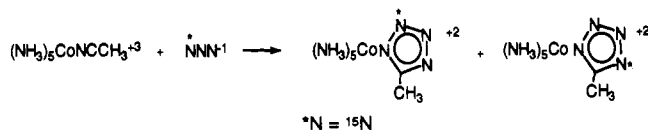
if a few drops of  $\text{D}_2\text{O}$  are added to the  $\text{DMSO}-d_6$ , indicating easily exchangeable (relatively acidic) protons. The natural-abundance  $^{15}\text{N}$  NMR spectrum of this complex is shown in Figure 1 as spectrum B. For comparison, a representation of the  $^{15}\text{N}$  NMR spectrum of the starting material, N2-bonded (5-cyanotetrazolato)pentaamminecobalt(III), adapted from ref 6 is shown as spectrum A along with the peak assignments ascribed to the ligand from the labeling studies given in that reference.<sup>6</sup> These and subsequent spectra are displayed in the region of the tetrazole ring nitrogens only. The ammine nitrogen signals are far upfield and, with the exception of the derivative of the 5-cyanotetrazole complex, relate no structural or mechanistic information. There are five such upfield peaks for the 5-cyanotetrazole derivative, but their unambiguous assignment has not been achieved at this time, and will not be discussed further in this report.

**Natural-Abundance and  $^{15}\text{N}$ -Labeled N1-Bonded (5-Methyltetrazolato)pentaamminecobalt(III).** The synthesis and characterization of this complex in the N1-bonded form *via* the attack of azide ion on the acetonitrile complex of pentaamminecobalt(III) have been reported previously.<sup>1</sup> The natural-abundance  $^{15}\text{N}$  NMR spectrum of the complex is shown as spectrum C in Figure 1. The method of synthesis suggests that if azide enriched with  $^{15}\text{N}$  at the terminus is utilized in the synthesis, then enrichment of  $^{15}\text{N}$  will occur specifically at ring sites 2 and 4 (50% of the product molecules with enrichment at site 2, the other 50% at position 4, and no molecules with two labeled nitrogens). This synthetic route is outlined in Scheme II. When



**Figure 2.**  $^{15}\text{N}$  NMR spectra of N1-bonded (5-methyltetrazolato)-pentaamminecobalt(III), the reactant R, at various stages of the linkage isomerization to the N2-bonded complex, the product P.

#### Scheme II



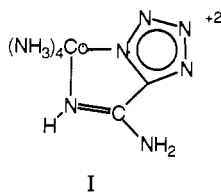
this approach was taken (see Experimental Section), a complex with  $^{15}\text{N}$  NMR spectrum D in Figure 1 was obtained. Allowing this complex to isomerize to the N2-bonded form for 6 linkage isomerization half-lives in  $\text{DMSO}-d_6$  produced a complex with spectrum E in Figure 1. Allowing an identically prepared enriched sample to isomerize in water for 6 half-lives, followed by precipitation with sodium perchlorate and dissolution in  $\text{DMSO}-d_6$ , produced a complex with spectrum F in Figure 1. Shown in Figure 2 are a series of  $^{15}\text{N}$  NMR spectra of the specifically labeled complex taken in  $\text{DMSO}-d_6$  at various time intervals during the first few half-lives for isomerization in DMSO.

#### Discussion

**Characterization of the 5-Cyanotetrazole Complex Derivative.** Visible and infrared spectra as well as elemental analysis of the complex formed by heating the N2-bonded (5-cyanotetrazolato)-

pentaamminecobalt(III) complex in DMSO indicate that the tetrazole ring is preserved while the cyano group has undergone modification. The spectral evidence also supports an N1-bonded complex. The unusually complex proton NMR spectrum indicates that the product is no longer a simple pentaamminecobalt(III) complex. While ample data exist for the isomerization of N1-bonded tetrazole complexes to less hindered N2-bonded forms,<sup>1-4</sup> the formation of an N1-bonded complex from an N2-bonded precursor, which seems to be required here, has not been previously reported for cobalt(III) tetrazolato complexes. Seemingly, identification of this complex could prove somewhat ambiguous were it not for the fact that its crystal structure had previously been reported by Graeber and Morosin,<sup>5</sup> who showed the complex to be a chelated, N1-bonded amidine complex. However, no previous literature has appeared discussing the synthesis, spectral properties, or bulk purification of the complex.

Amidine formation between a coordinated amine and a nearby cyano group of a ligand has been reported in several previous studies.<sup>12-15</sup> In those cases, amidine formation was rather facile in moderately basic solution (pH 8-10), requiring reaction times of tens of seconds in most cases. Facile formation of the amidine is clearly not the case here. However, since linkage isomerization of the starting material to the thermodynamically unfavorable N1-bonded form is necessary for the cyano group to be in position for reaction with one of the *cis* amines of the pentaamminecobalt(III) moiety, the slow rate of formation is not surprising. Amidine formation is probably just as facile in this system as in others, with linkage isomerization being rate determining. The red shift in the visible spectrum of this "amidine chelate" is typical of this functional group.<sup>15</sup> The 8.55 ppm proton resonance can be assigned to the exocyclic (uncoordinated) nitrogen protons,<sup>12</sup> and this nitrogen has two protons attached, which is typical of such linkages.<sup>12-15</sup> The structure of the "amidine chelate" is shown in I.



I

The percent yield for the synthesis of the amidine chelate compound reported here (see Experimental Section) is rather low, and unreacted starting material and unidentified decomposition products are major impurities in the synthesis. The latter can be removed for the most part by filtration. However, the product and starting material are not so easily separated. Cation exchange of a mixture of amidine chelate and 5-cyanotetrazolato complexes of SP-Sephadex does not result in efficient separation of the two 2+ complexes. Therefore, we make the final product mixture 1 M in sodium hydroxide and allow this solution to sit for 1 h before filtration and chromatography. This amount of time in the base is sufficient to convert any residual starting material to an N2-bonded pentaamminecobalt(III) complex of tetrazole-5-carboxylate<sup>16</sup> which is a 1+ complex and, hence, is easily separated from the amidine chelate complex. We should note that the use of triethylamine in the synthesis is not necessary for production of the amidine chelate complex. Simple heating of a DMSO solution of the 5-cyanotetrazolato complex will lead

to formation of the product, but longer reaction times (3-6 days at 85 °C) are necessary for a significant yield.

**<sup>15</sup>N NMR Spectra of N1-Bonded Tetrazole Complexes.** Since N1-bonded tetrazole complexes tend to isomerize to their N2-bonded forms in solution,<sup>1-4</sup> obtaining natural-abundance <sup>15</sup>N NMR spectra of such compounds is difficult at best since many thousands of pulses are usually necessary for a reasonable signal-to-noise ratio. Fortunately, the (5-methyltetrazolato)pentaamminecobalt(III) complex has a half-life for linkage isomerization of about 100 h at ambient temperature in water,<sup>2</sup> and thus, it is an excellent candidate for such a study. At the NMR probe temperature of 21.5 °C, the half-life for isomerization in DMSO is closer to 300 h.<sup>4</sup> The "amidine chelate" complex discussed above provides another suitable complex for study since it is "locked" into the N1-bonding mode by chelation. In order to achieve complex concentrations as high as possible, we opted to work with perchlorate salts of all complexes involved and use dimethyl sulfoxide (DMSO) as the solvent for NMR studies. Concentrations in excess of 1 M were achieved under these conditions.

Uncoordinated 5-substituted tetrazoles or their sodium salts show two resonances for their ring nitrogens, one near 0 ppm ( $\pm 15$  ppm vs nitromethane) for the equivalent nitrogens at ring positions 2 and 3 and a second in the -50 to -70 ppm range for nitrogens 1 and 4.<sup>6,7</sup> For sodium 5-methyltetrazolate, for example, these resonances appear at -0.47 and -69.34 ppm for the N2,N3 and N1,N4 nitrogens respectively.<sup>7</sup> Coordination to cobalt(III) *via* either nitrogen 1 or nitrogen 2 will produce inequivalence in all four ring nitrogens, leading to four resonances.

The natural-abundance <sup>15</sup>N NMR spectra of two N1-bonded complexes are shown in Figure 1B for the amidine chelate and in Figure 1C for the (5-methyltetrazolato)pentaamminecobalt(III) complex. The spectra are atypical of the spectra of N2-bonded tetrazolato ring systems published previously,<sup>6,7</sup> such as spectrum A in Figure 1 from ref 6, for the N2-bonded (5-cyanotetrazolato)pentaamminecobalt(III) complex. While both N1 and N2 bondings produce a broadened and upfield shifted resonances for that nitrogen directly bonded to cobalt, spectra of the N2-bonded species exhibit two other resonances 20 ppm or more upfield of nitromethane while the fourth nitrogen signal is downfield of the reference.<sup>6,7</sup> The N1-bonded complexes, on the other hand, show only one other resonance upfield with the ligated nitrogen, while the final two signals are near and downfield from the nitromethane shift reference. The severe broadening of the nitrogen directly bound to cobalt is no doubt due to the quadrupole moment of the <sup>59</sup>Co nucleus ( $I = 7/2$ ).

Assignments of the resonances in the N1-bonded spectrum of the 5-methyltetrazolato complex is facilitated by the terminally labeled azide attack on coordinated acetonitrile, which produces regiospecific <sup>15</sup>N enrichment at positions 2 and 4 of the tetrazole ring. The spectrum of the product resulting from this treatment is given in Figure 1 as spectrum D. Analysis of this spectrum permits assignment of the resonance near 0 ppm to the N2 ring nitrogen, and thus, the N3 resonance can be assigned to the 12 ppm peak in the natural-abundance spectrum (Figure 1C). The peak near -50 ppm for the enriched sample is due to the N4 nitrogen, as indicated by the free-ligand peak positions. As discussed in the preceding paragraph, the broad resonance at ca. -167 ppm is due to the N1 nitrogen bonded directly to the cobalt(III). Given the great similarity of the amidine chelate spectrum (Figure 1B) to that of the N1-bonded 5-methyltetrazolato complex, identical assignments seem justified. Hence, N3 is assigned to the 28 ppm resonance, N2 to the peak at 0.1 ppm, N4 to the -53 ppm peak, and N1 to the broad resonance at ca. -147 ppm.

**Transition-State Considerations for Tetrazole Linkage Isomerization.** Evidence supplied by previous kinetic studies of the N1-to-N2 linkage isomerization process of (tetrazolato)pentaam-

(12) Buckingham, D. A.; Foxman, B. M.; Sargeson, A. M.; Zanella, A. J. *Am. Chem. Soc.* **1972**, *94*, 1007.

(13) Nolan, K. B.; Hay, R. W. *J. Chem. Soc., Dalton Trans.* **1974**, 914.

(14) Buckingham, D. A.; Clark, C. R.; Foxman, B. M.; Gainsford, G. J.; Sargeson, A. M.; Wein, M.; Zanella, A. *Inorg. Chem.* **1982**, *21*, 1986.

(15) Geue, R. J.; Springborg, J.; Sargeson, A. M. *Acta Chem. Scand., Ser. A* **1987**, *41*, 158.

(16) Lopez de la Vega, R. Ph.D. Dissertation, University of Miami, Coral Gables, FL, 1985.

minecobalt(III) complexes supports an intramolecular process rather than a dissociative ion-pair type of process. Among the evidence against an ion-pair mechanism is the fact that no detectable amounts of aquopentaamminecobalt(III) complex are formed during the isomerization process.<sup>1</sup> Also, the rate constants for isomerization of the 5-methyltetrazolato complex at ionic strength 1.0 M and near ionic strength 0 are nearly identical.<sup>2,4</sup> A substantial increase in the rate constant with increased ionic strength would be expected for a dissociative process. Also, studies in 11 different solvents support no radical change in mechanism from one solvent to another.<sup>4</sup> A comparison of the spectra resulting from isomerization of the labeled N1-bonded starting material in DMSO (Figure 1E) and water (Figure 1F) supports this conclusion. Hence, the mechanistic results reported herein for isomerization in DMSO are, we feel, reflective of the process that occurs in water as well as common organic solvents.

Several types of intramolecular transition states can be visualized for the N1-to-N2 linkage isomerization process. The most straightforward of these would be an  $\eta^2$  transition state involving N1 and N2. Such a transition state is appealing not only because it requires a minimum of molecular motion between the two bonding modes but also because this type of  $\eta^2$  bonding has been reported for the isoelectronic pyrazolate ligand on uranium(IV).<sup>17</sup> However, since the tetrazolato ligand is isoelectronic with the cyclopentadienide ring, an  $\eta^5$  transition state seems to deserve consideration as well. The recent assertion that  $\eta^5$ -tetrazolate ligands enjoy a solution existence in manganese(I) complexes only adds to the attractiveness of such a transition-state structure.<sup>18</sup> Finally, to be complete, various  $\eta^3$  transition states involving the N1 nitrogen should be considered. An  $\eta^3$ -(N1,C,N4) transition state would not lead to final N2-bonded product and, hence, can be ignored. However, an  $\eta^3$ -(C,N1,N2) and an  $\eta^3$ -(N1,N2,N3) transition state would equally well produce an N2-bonded product.

Several of the above considered transition states can be distinguished from others by following the <sup>15</sup>N spectrum of the specifically labeled N1 complex as it isomerizes to the N2-bonded product. The  $\eta^5$  transition state should produce a product with totally scrambled enriched ring nitrogens (i.e., four enriched signals) since bonding to cobalt(III) in the final product could be at either of the equivalent nitrogens N2 and N3, and N2 or N4 being enriched in the N1-bonded starting material. The  $\eta^2$  transition state, however, would produce an N2-bound product complex with enriched-sample signals at only the N4 and N2 ring sites, i.e., two enriched-sample signals with the latter N2 signal broadened due to interaction with the quadrupole moment of the directly bound cobalt(III). The two  $\eta^3$  transition states considered in the previous paragraph would also fall into one of these two categories. An  $\eta^3$ -(C,N1,N2) transition state would produce an N2-bound product with two enriched-sample signals identical to those produced by the  $\eta^2$  transition state. The  $\eta^3$ -(N1,N2,N3) transition state, however, would produce four enriched-sample signals in the spectrum of the N2-bonded product, just as would be observed for the  $\eta^5$  transition state.

**Analysis of Figure 2 in Terms of Transition-State Structure.** The spectra of the enriched species in Figure 1 indicate that the initial two signals for the N1-bound complex produce four enriched-sample signals (i.e., scrambled nitrogen signals) after approximately 6 isomerization half-lives in solution. In light of the discussion given in the previous section, either the  $\eta^5$  or the  $\eta^3$ -(N1,N2,N3) transition state would seem to be implicated. However, if the isomerization process is examined at various time intervals over the course of the reaction, different conclusions are required. Figure 2 illustrates just such a study obtained over a 600-h period.

Spectra in Figure 2 suggest that during the first 126 h of isomerization (a half-life for isomerization in DMSO at the probe temperature of 21.5 °C is 305 h<sup>4</sup>) the two enriched-sample N1 peaks at 0 and -52 ppm produce two new N2 complex enriched-sample peaks at -44 and -98 ppm, the latter quite broad as expected for the N2 nitrogen bound to Co(III). It is only after some 250 h that a third and a fourth enriched-sample signal appear at approximately 10 and -70 ppm. These latter two peaks then grow in size and eventually acquire the intensity of the two N2 product peaks that were the first to appear. Some of this intensity gain is clearly at the expense of the -44 and -98 ppm peaks. These observations are indicative of a two step-process. The first step is isomerization of the N1-bonded complex to its N2-bonded form *via* a transition state that produces only two enriched-sample signals, that is, either the  $\eta^2$  or the  $\eta^3$ -(C,N1,N2) transition state discussed in the previous section. However, this N2 product then proceeds to scramble its nitrogens, leading to the observation of all four ring nitrogen signals from the original two. In other words, the N2-bonded complex undergoes an N2-to-N3 linkage isomerization. Of course, without the specific <sup>15</sup>N labels, such a process would go undetected since the N2- and N3-bound products are in fact identical. Hence, the occurrence of this process had never been detected in previous visible or infrared studies of these systems. A qualitative inspection of Figure 2 indicates that this "fluxional" N2 complex process occurs on a time scale comparable to that of the N1-to-N2 linkage isomerization reaction.

The appearance of several minor peaks, especially in the latter stages of the Figure 2 sequence, deserves some comment. It is not apparent what these peaks represent, other than some minor impurity or impurities due to complex decomposition. Most were not seen in the Figure 1 N2 spectra (E and F) which were obtained over even longer periods of time. However, the sample used to obtain the spectra in Figure 2 received harsher treatment than those used for Figure 1. Due to scheduling considerations for the VXR-400 instrument, the samples employed for Figure 2 spectra were often frozen for 1 or 2 weeks to quench linkage isomerization until another schedule run date occurred. Each sample was then rapidly thawed and the time sequence for solution isomerization resumed. The samples for spectra E and F, on the other hand, were never subjected to repeated freeze/thaw cycles. However, even these samples receiving gentler treatment show three minor peaks that are unexplained. These peaks could never totally be eliminated, although they could be suppressed when the acetonitrile used for the enriched N1 complex synthesis was repeatedly distilled before use. Unfortunately, we discovered this fact only after a significant amount of our enriched azide had been committed to synthesis, and thus, we present herein our spectra complete with "warts".

As mentioned above, our results and interpretation lead to elimination of the  $\eta^3$ -(N1,N2,N3), the  $\eta^3$ -(N1,C,N4), and the  $\eta^5$  transition states for linkage isomerization. Of the two transition states consistent with our observations and analysis, the  $\eta^3$ -(C,N1,N2) and the  $\eta^2$ -(N1,N2) states, we favor the  $\eta^2$  state for its simplicity, minimal requirement for atomic movement, and similarity to the known pyrazolate/uranium complex bonding mode.<sup>17</sup> However, the present study is not able to distinguish one from the other.

The subsequent "scrambling" reaction of the N2-bonded complex was a surprise to us. Clearly, the free energy change for the reaction is zero. The nature of the process and the nitrogen labeling positions do not allow us to comment on any possible transition state for the rearrangement, although the similar rate of the N1-to-N2 process would suggest a similar pathway, i.e., another  $\eta^2$  transition state. Such processes might actually be rather commonplace in Co(III) chemistry but difficult to detect

(17) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* 1981, 20, 1553.

(18) John, E. O.; Willett, R. D.; Scott, B.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* 1989, 28, 893.

due to the synthetic problems encountered in the required isotopic labeling procedures such as those experienced with the nitrito system.<sup>10</sup>

**Implications Concerning Peak Assignments for N2-Bonded Complexes in Light of the Isomerization Process.** The initial <sup>15</sup>N NMR investigation of an N2-bonded tetrazolato complex of pentaamminecobalt(III) led to the ring nitrogen assignments shown in Figure 1A.<sup>6</sup> The specific labeling experiments of that study permitted an unambiguous distinction between the signals of the N1/N4 pair of nitrogens and the N2/N3 nitrogen pair. Also, because of the severe broadening associated with the Co(III)-bound N2 nitrogen, the N2 and N3 signals could be confidently distinguished. Thus, the N2-bonding mode of the complex was confirmed. However, the distinction between the N1 and N4 nitrogen signals was less direct. The assignment of the -30 ppm signal to N1 and the -47 ppm signal to N4 was concluded from a consideration of the adjacent-atom  $\alpha$  effect on the chemical shifts of similar nitrogen-containing organics with alkyl (not transition metal) substituents.<sup>19-21</sup> Our present study indicates that these N1 and N4 assignments for the N2-bonded 5-methyltetrazolato complex need to be reversed. As the specifically labeled N1-bonded complex begins to isomerize to the N2-bonded complex, signals at -44 and -98 ppm appear. Since, as mentioned in the previous section, the broad -98 ppm signal is easily assigned to the Co(III)-bound N2 nitrogen, the -44 ppm peak then must be due to the only other labeled nitrogen position, the N4 nitrogen. Hence, the peak at -69 ppm in the natural-abundance spectrum must be due to the N1 nitrogen. Assignment based on ref 6 would have reversed these assignments and clearly would have been in error. Of course, this discussion strictly applies only to the 5-methyltetrazolato complex of this study, not to the 5-cyanotetrazolato complex of ref 6. One cannot be absolutely certain that the N1/N4 shift patterns are identical in the two. However, it is now clear that the  $\alpha$ -effect analysis fails with the 5-methyltetrazolato complex, and hence, doubt as to the correctness of the N1/N4 nitrogen assignments exists for the 5-cyanotetrazolato complex<sup>6</sup> as well as other N2-bonded-complex spectra that were assigned on the basis of that 1983 study.<sup>7</sup>

## Experimental Section

**Physical Measurements.** Ultraviolet and visible spectra were recorded on a Cary 17 spectrophotometer. The infrared spectra, as KI pellets, were recorded on a Perkin-Elmer 599 spectrophotometer. A Radiometer Model 26 pH meter equipped with a glass combination electrode (calomel

reference) was used to obtain all pH measurements. Since many solutions contained perchlorate, NaCl was substituted for KCl in the electrode. Calibration was achieved with Fisher Certified standard buffers at two pH values. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Routine proton NMR spectra were obtained on a Hitachi Perkin-Elmer R-600 60-MHz FT NMR instrument. <sup>15</sup>N NMR spectra were recorded on a Varian VXR-400 multinuclear instrument operating at a frequency of 40.543 MHz at the ambient probe temperature of 21.5 °C. A pulse width of 25  $\mu$ s produced a 90° flip angle. Approximately 40 000 transients were averaged for natural-abundance spectra, while enriched samples required only 4000 transients. All <sup>15</sup>N spectral acquisitions were obtained from either perchlorate salts (Figure 1 spectra) or triflate salts (Figure 2 spectra) of the complexes utilizing DMSO-*d*<sub>6</sub> as the solvent in 10-mm tubes containing ca. 0.05 M tris-(acetylacetonato)chromium(III) as a relaxation reagent. Chemical shifts recorded in Figure 1 are thought to be accurate to ca.  $\pm 1$  ppm except for peaks in low signal to noise spectrum (C) and quadrupole-broadened peaks which are ca.  $\pm 3$  ppm.

**Synthesis.** N2-bonded (5-cyanotetrazolato)pentaamminecobalt(III) bromide (CP bromide) was synthesized and purified as described previously<sup>6</sup> by utilizing 5-cyanotetrazole kindly supplied by Dr. John Fronabarger (Unidynamics Phoenix, Inc.) and NaBr for recrystallization. Sodium azide, 99% enriched in <sup>15</sup>N at the terminal nitrogen, was purchased from ICN Biomedicals, Inc., Stable Isotopes Division, and was used as received.

**(Tetrazole-5-carboximidamido-N1,N')tetraamminecobalt(III) Bromide.** CP bromide (0.20 g) was dissolved in a minimum of dimethyl sulfoxide (ca. 5 mL), and 2 or 3 drops of triethylamine were added. This solution was placed in a sealed tube and heated to 85 °C overnight (ca. 14 h). At the end of the heating period, the solution was diluted to 20 mL and made 1 M in sodium hydroxide. After sitting for 1 h, this solution was filtered to remove a dark precipitate of decomposition product, the filtrate was diluted to ca. 500 mL, and the resulting solution was charged onto a column of SP-Sephadex. Elution with 0.05 M NaCl moved out a minor pale yellow band of the N2-bonded tetrazole-5-carboxylate complex. The major orange band was brought to the bottom of the column with 0.20 M NaCl and eluted off in concentrated form with 2 M sodium trifluoromethanesulfonate. Addition of solid NaBr to this concentrated solution induced precipitation of the chelated product which was filtered off, washed with methanol and then diethyl ether, and dried *in vacuo*. A yield of 0.09 g of product (45%) was obtained. When we scaled-up this preparation and/or used sodium perchlorate for precipitation, yields invariably were smaller (10–20%).

Anal. Calcd for CoC<sub>2</sub>H<sub>15</sub>N<sub>10</sub>Br<sub>2</sub>: C, 6.04; H, 3.80; N, 35.20; C:N, 0.172. Found: C, 6.15; H, 3.85; N, 34.92; C:N, 0.176. Visible spectrum:  $\epsilon_{473}$  92 M<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{332}$  115 M<sup>-1</sup> cm<sup>-1</sup> (in H<sub>2</sub>O);  $\epsilon_{473}$  92 M<sup>-1</sup> cm<sup>-1</sup>,  $\epsilon_{332}$  114 M<sup>-1</sup> cm<sup>-1</sup> (in 0.10 M HCl);  $\epsilon_{478}$  105 M<sup>-1</sup> cm<sup>-1</sup> (in 0.10 M NaOH).

**Acknowledgment.** We are indebted to Dr. David M. Hudson for <sup>15</sup>N NMR spectra obtained on the VXR-400 instrument. We also thank Dr. John Fronabarger of Unidynamics Phoenix, Inc., for a sample of 5-cyanotetrazole.

(19) Witanowski, M.; Stefaniak, L.; Januszewski, Grabowski, Z. *Tetrahedron* **1972**, *28*, 637.

(20) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 2495.

(21) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 4908.