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Note

Formation of an observable intermediate during the reduction of $[Co^{(III)}(NH_3)_5CN]^{2+}$ by $^{\bullet}CR^1R^2(OH)$ radicals

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Abstract

$^{\bullet}CR^1R^2OH$, $R^i = CH_3$ or H, react with the complex $[Co^{III}(NH_3)_5CN]^{2+}$ to form an observable intermediate probably via bonding to the nitrogen of the cyanide. This intermediate isomerizes to form a second intermediate. The second intermediate decomposes into $Co^{2+}(aq)$, $5NH_4^+$, CN^- and R^1R^2CO. The plausible structures of the intermediates are discussed. The radicals $^{\bullet}CH^3$, $^{\bullet}CH_2CHO$, $^{\bullet}CH(OH)CO_2^-$, $^{\bullet}CH_2C(CH_3)_2OH$, $CO_2^{\bullet -}$ and $CH_3O_2^{\bullet}$ are considerably less reactive towards this complex, the formation of intermediates in their presence is not observed.

Keywords: Pulse radiolysis; Cobalt complex; Alkyl radicals

1. Introduction

The reduction of $[Co^{III}(NH_3)_5X]^{2+}$, X = halides and pseudo halides, by alkyl radicals and by $^{\bullet}CR^1R^2OH$ radicals proceeds via the inner sphere mechanism [1–4]. Even the reduction of $Co^{III}(NH_3)_6{}^{3+}$ by the $^{\bullet}CR^1R^2OH$ radicals was shown to proceed via the inner sphere mechanism [5]. However, in none of these reactions was an intermediate observed [5,6].

It seemed reasonable that the reduction of $[Co^{III}(NH_3)_5CN]^{2+}$ by the same radicals will also proceed via the inner sphere mechanism and that intermediates of the type $(NH_3)_5Co{-}\dot{C}{=}N{-}CR^1R^2OH^{2+}$, if formed, might have a longer life-time and therefore be observable. Indeed, the results corroborate this assumption.

2. Experimental

The complex Co^{III}pentaaminocyano perchlorate, $[Co(NH_3)_5CN](ClO_4)_2$, was synthesized according to the procedure described in the literature [7,8]. It was characterized by the typical UV–vis d–d absorption bands, at 440 nm (57.0 M^{-1} cm^{-1}) and 327 nm (53.9 M^{-1} cm^{-1}) in good agreement with its reported spectrum [8].

All chemicals and gases used in the study were of A.R. grade, supplied by Aldrich, Fluka, Merck or Maxima. The solutions were prepared using distilled water that was further purified using a millipore Milli-Q system. The final resistance was better than 10 MΩ/cm.

The pH was measured using a Corning 220 pH meter. UV–vis spectra were measured using a 8452A HP diode-array spectrophotometer.

The radicals studied were produced using ionizing radiation techniques (pulse radiolysis [9] and ^{60}Co γ source). The pulse radiolysis technique employed the Varian Linear Electron Accelerator of the Hebrew University, which produces 5 MeV, 200 mA short electron pulses of 0.5–1.5 μs (delivered dose 6.5–19.5 Gray/pulse). The second irradiation source was a ^{60}Co γ radiation source (1.1 MeV photons), Noratom 3500 unit, (delivered dose rate of 6.5 Gray/min).

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Deaeration of the solutions was achieved by bubbling the desired gas through the solution for 20 min. Transfer and dilution of deaerated solutions were carried out using the syringes technique [10].

The yield of $Co^{2+}{}_{aq}$ was determined by a colorimetric method at 620 nm [11].

Formaldehyde was determined by a colorimetric method [12] of its yellow complex with acetyl acetone (diacetyl-dihydro lutidine) at 412 nm.

Ethane and methane were determined using a Varian 3700 gas chromatograph equipped with a FID detector, the separation of the gases was carried out on a Poropaq Q 1/8″, 9′ column with helium as the carrier gas.

2.1. Production of the α hydroxy and other aliphatic radicals

When water is exposed to ionizing radiation the process occurring is [13]

$$H_2O \overset{e^-,\gamma}{\rightarrow} e^-{}_{aq}(2.65),\ {}^{\bullet}OH(2.65),\ {}^{\bullet}H(0.65),\ H_2O_2(0.75),\ H_2(0.45) \qquad (1)$$

(in parentheses are given the relative yields in G values; G value is the number of product species produced per 100 eV energy absorbed by the sample). If the irradiated water is saturated by N_2O (0.022 M) and contains 0.1–1 M of the appropriate alcohol $HCR^1R^2(OH)$, the following reactions occur within less than 1 μs:

$$N_2O + e^-{}_{aq} + H^+ \rightarrow {}^{\bullet}OH + N_2 \quad k = 8.9\times10^9\ M^{-1}\ s^{-1}\ [14] \qquad (2)$$

$$\begin{aligned}&{}^{\bullet}OH/{}^{\bullet}H + HCR^1R^2(OH) \rightarrow {}^{\bullet}CR^1R^2(OH) + H_2O/H_2\\ &k_{OH} = (0.8\text{–}2)\times10^9\ M^{-1}\ s^{-1}\ [14]\\ &k_H = (2\text{–}70)\times10^6\ M^{-1}\ s^{-1}\ [14]\end{aligned} \qquad (3)$$

When the organic solute is $(CH_3)_2SO$ methyl radicals are formed via [15]

$$^{\bullet}OH + (CH_3)_2SO \rightarrow (CH_3)_2\dot{S}O(OH) \quad k = 7.0\times10^9\ M^{-1}\ s^{-1} \qquad (4)$$

followed by

$$(CH_3)_2SO(OH) \rightarrow {}^{\bullet}CH_3 + (CH_3)_2SO(OH) \quad k = 1.5\times10^7\ s^{-1} \qquad (5)$$

If the $(CH_3)_2SO$ solution is saturated with 80% N_2O/20% O_2, then the methyl radicals are transformed into methylperoxyl radicals via

$$^{\bullet}CH_3 + O_2 \rightarrow CH_3O_2^{\bullet} \quad k = 1.5\times10^9\ M^{-1}\ s^{-1}\ [16] \qquad (6)$$

Thus, in less than 1 μs from the end of the electron pulse (or the absorption of the γ radiation) all hydroxyl radicals, hydrated electrons and hydrogen atoms are converted into the desired aliphatic radicals which are the only reactive species present in the solution.

3. Results and discussion

3.1. Reaction of $[Co(NH_3)_5CN]^{2+}$ with the hydrated electron e^-_{aq}

In order to determine whether $[Co(NH_3)_5CN]^+$ absorbs light in the UV–vis region, the hydrated electron $e^-{}_{aq}$ has been used as the reducing reagent. Helium saturated solutions containing 1×10^{-4} M of $[Co(NH_3)_5CN]^{2+}$ and 1.0 M of $C(CH_3)_3OH$ in the pH range 3–6 (achieved by addition of 0.050 M phosphate buffer) were irradiated by a short electron pulse from the linear accelerator. (The radicals ${}^{\bullet}CH_2C(CH_3)_2(OH)$ produced by H abstraction from the $(CH_3)_3COH$ by hydroxyl radicals [17] do not, react with the complex, see below.) No unstable intermediates absorbing light in the UV–vis region were observed. The only final product detected was $Co^{2+}{}_{aq}$ and its G value was determined to be 3.0 ± 0.6, which equals the combined yields of the hydrated electrons and hydrogen atoms, thus, proving that the hydrated electrons react via:

$$[Co^{III}(NH_3)_5CN]^{2+} + e^-{}_{aq} \rightarrow Co(NH_3)_5CN^+ \overset{5H^+}{\rightarrow} Co^{2+}{}_{aq} + CN^- + 5NH_4^+ \qquad (7)$$

and that the complex $Co(NH_3)_5CN^+$ is either very unstable with a half life shorter than the detection limit, 1 μs, and/or that it has no absorption band with $\varepsilon \geqslant 100\ M^{-1}\ cm^{-1}$ in the 270–600 nm region. Both these possibilities are in accord with the expected properties of the Co(II) complex.

3.2. Reaction of $[Co(NH_3)_5CN]^{2+}$ with ${}^{\bullet}CH_2OH$, ${}^{\bullet}CH(CH_3)OH$ and ${}^{\bullet}C(CH_3)_2OH$

When N_2O saturated solutions containing $(1\text{–}10)\times10^{-4}$ M $[Co(NH_3)_5CN]^{2+}$ at the pH range 3–6 (phosphate buffer 0.050 M) containing (0.10–1.0) M of the appropriate alcohol (methanol, ethanol or 2-propanol) are irradiated by a short pulse from the linear accelerator, the formation of unstable intermediates in the 5–40 μs time range is observed. These intermediates decompose to the final stable products within 1000–4000 μs. A typical kinetic plot for the reaction of the hydroxymethyl radical, ${}^{\bullet}CH_2OH$, with the complex is presented in Fig. 1.

The kinetics of formation of the unstable intermediates obeys pseudo first-order rate laws with a linear dependence on the concentration of the cobalt (III) complex. The rates are independent on the alcohol concentration, pH, phosphate buffer concentration, and

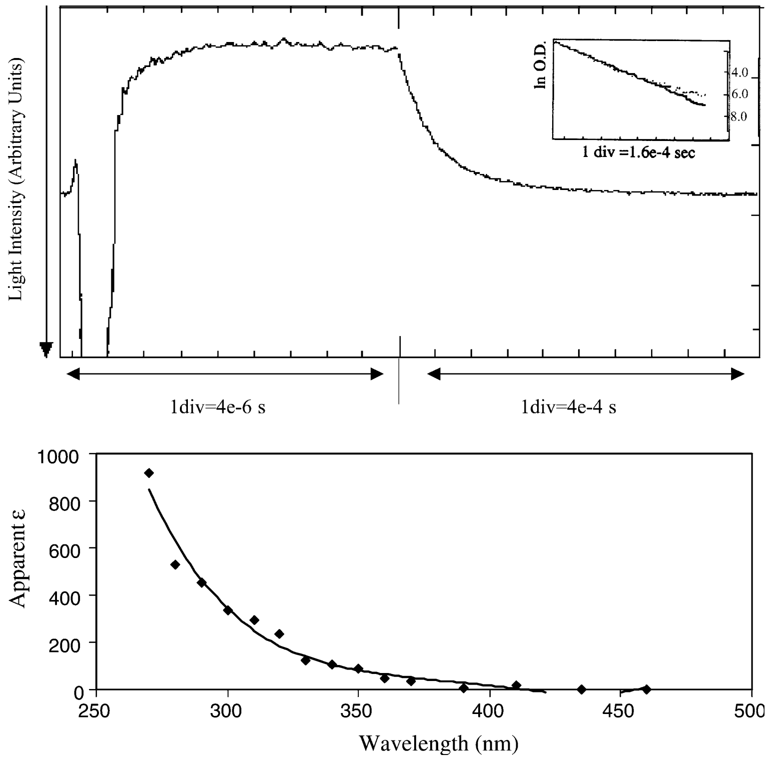
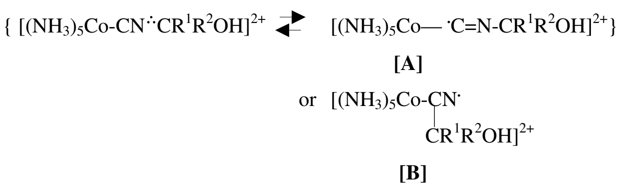


Fig. 1. Kinetic changes, measured at 290 nm (inset: first-order plot) after a short electron pulse (0.5 μsecond), was delivered to an N_2O saturated solution containing 0.10 M methanol, 3.0×10^{-4} M $[Co(NH_3)_5CN]^{2+}$ and 0.050 M phosphate buffer at pH 3.0. (a) Absorption spectrum of the intermediate formed by the $^{\bullet}CH_2OH$ radicals. N_2O saturated solution contained 0.1 M methanol, 3×10^{-4} M $[Co(NH_3)_5CN]^{2+}$, 0.05 M phosphate buffer at pH 3.5.

wavelength of measurement or pulse intensity. The results clearly show that the formation of the unstable intermediates is due to the reaction of the α-hydroxyalkyl radical with the cobalt complex:

$$[Co^{III}(NH_3)_5CN]^{2+} + {}^{\bullet}CR^1R^2(OH) \rightarrow \text{Intermediate I} \qquad (8)$$

It is proposed that the intermediate, formed in reaction (8), is $(NH_3)_5Co^{III}\text{–}\dot{C}N\text{–}CR^1R^2(OH)^{2+}$. It cannot be $Co(NH_3)_5CN^+$ as this intermediate does not absorb in this spectral region (see above). It is suggested that the carbon centered radical binds to the cyano ligand as no intermediates are observed in the reactions of these radicals with $Co(NH_3)_6{}^{3+}$ (5). Thus, the transient could be either:



$$\{[(NH_3)_5Co\text{-}CN^{\cdot\cdot}CR^1R^2OH]^{2+} \rightleftarrows [(NH_3)_5Co\text{—}{}^{\cdot}C{=}N\text{-}CR^1R^2OH]^{2+}\}$$

[A]

$$\text{or } [(NH_3)_5Co\text{-}\underset{\displaystyle |\atop \displaystyle CR^1R^2OH]^{2+}}{C}N^{\cdot}$$

[B]

In order to determine the specific rates of reaction (8) for the three radicals, the observed pseudo first-order rate constants were measured at different complex concentrations and the dependence of k_{8ob} on $[\{Co^{(III)}(NH_3)_5CN\}^{2+}]$ was plotted, Fig. 2 (for the hydroxymethyl and hydroxyisopropyl radicals). The slopes of these lines are the specific rate constants of reaction (8) k_8: $(9 \pm 2) \times 10^7$, $(6 \pm 1) \times 10^7$ and $(6 \pm 1) \times 10^7$ $M^{-1}\,s^{-1}$ for $^{\bullet}CH_2OH$, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$, respectively.

It is interesting to note that extrapolation to zero complex concentration results in a large intercept for all three intermediates, thus pointing out that reaction (8) is an equilibrium process:

$$[Co^{III}(NH_3)_5CN]^{2+} + {}^{\bullet}CR^1R^2(OH) \leftrightarrows \text{Intermediate} \qquad (8)$$

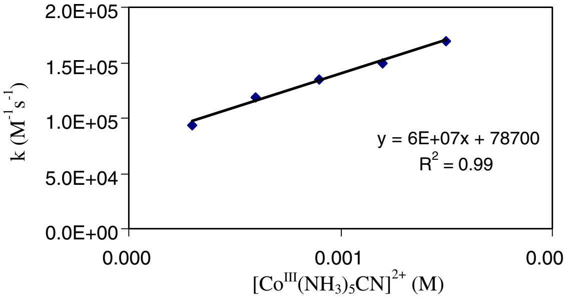


Fig. 2. Dependence of k_{obs} vs. [complex] for the reaction of the complex with $^{\bullet}C(CH_3)_2OH$ at pH 2.5, N_2O saturated solutions containing 1 M alcohol and $[x] \times 10^{-3}$ M complex.

where k_{-8} can be evaluated from the intercepts in Fig. 2: $(17 \pm 5) \times 10^4$, $(10 \pm 3) \times 10^4$ and $(8 \pm 2) \times 10^4\ \mathrm{s}^{-1}$ for $^{\bullet}CH_2OH$, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$, respectively. The contribution due to the second-order bimolecular radical–radical reactions, reaction (9), is only $\sim 1 \times 10^4\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and as such cannot account for the much higher values observed.

$$2^{\bullet}CR^1R^2(OH) \rightarrow \text{products}$$
$$2k_9 = (1\text{–}3) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}\ [17,18] \qquad (9)$$

From these values the equilibria constants K_8 can be calculated: $(5 \pm 2) \times 10^2$, $(6 \pm 2) \times 10^2$ and $(7 \pm 3) \times 10^2\ \mathrm{M}^{-1}$ for $^{\bullet}CH_2OH$, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$, respectively.

The equilibria constants K_8 can also be calculated from the dependence of the $1/[\{Co^{III}(NH_3)_5CN\}^{2+}]$ values on $1/OD_{inf}$, Fig. 3. A linear dependence is observed and K_8 can be calculated, the values $(4.4 \pm 1.0) \times 10^2$, $(7.3 \pm 1.0) \times 10^2$ and $(5.3 \pm 1.0) \times 10^2\ \mathrm{M}^{-1}$ are the values obtained for $^{\bullet}CH_2OH$, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$, respectively. These values are in good agreement with those obtained from the direct kinetic measurements and are more accurate as the estimated error is much smaller.

The values of K_8 are not large and indicate that only ~10% of the radicals are transformed into the complex–radical intermediate via reaction (8) and that ~90% of the hydroxyaliphatic radicals are still present in the irradiated solutions.

The spectra of the three intermediates in the UV–vis region 270–600 nm have been measured and one is given for the hydroxymethyl intermediate, Fig. 1(a). One absorption band is observed at the UV but its maximum absorption peak could not be determined, $\lambda_{max} < 270$ nm. The extinction coefficient at 270 nm could be determined using the value of 440 M^{-1} for K_8 for $^{\bullet}CH_2OH$ (see above) and found to be very large $\varepsilon(270\ \mathrm{nm}) > 10\,000\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. This value indicates that it stems from an allowed electronic transition, probably a LMCT transition. Similar spectra, with similar molar absorption coefficients, were obtained for the intermediates formed by the $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$ radicals.

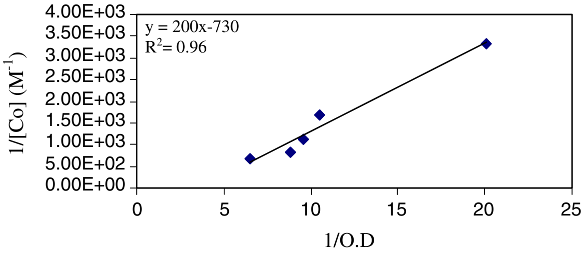


Fig. 3. Dependence of 1/[complex] vs. 1/OD for the reactions of the complex with $^{\bullet}CH_2OH$ at pH 2.5, N_2O saturated solutions containing 1 M alcohol and $[x] \times 10^{-3}$ M complex.

The decomposition of the intermediates has been measured (Fig. 1) and the kinetics also obeyed a first-order rate law for all three radicals. The rates are independent of the concentration of the cobalt (III) complex, the corresponding alcohol, the buffer, the pH or the pulse intensity and wavelength of measurement. The specific rate constants for the decomposition reaction (10):

$$[Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+}\ \text{intermediate} \rightarrow \text{products} \qquad (10)$$

were measured: $(6.0 \pm 0.9) \times 10^3$, $(5.0 \pm 0.9) \times 10^3$ and $(4.0 \pm 0.7) \times 10^3\ \mathrm{s}^{-1}$ for $^{\bullet}CH_2OH$, $^{\bullet}CH(CH_3)OH$ and $^{\bullet}C(CH_3)_2OH$, respectively. The fact that the decomposition of the complex radical intermediates obeys first-order kinetics is quite surprising. The only possibility that can explain it is that the equilibrium process is followed by an intramolecular fast step, $k_{11} > 2 \times 10^4\ \mathrm{s}^{-1}$ to yield a more stable intermediate, Intermediate II, reaction (11):

$$\underset{\text{Intermediate I}}{[Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+}} \rightarrow \underset{\text{Intermediate II}}{([Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+})'} \qquad (11)$$

The second intermediate decomposes to the final products. This conclusion is derived from the fact that the bleaching of absorption occurs in the ~2000 μs time range. If the absorption is that of the intermediate which is formed via reaction (8), then the dominant species in the solution will be the hydroxyalkyl radical (~90%, see above) and as the bimolecular decomposition, reaction (9), for the three α-hydroxyalkyl radicals is diffusion controlled $2k_9 = (1\text{–}3) \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$, i.e., the decomposition will obey second-order rate laws and terminate within less than a millisecond which is not the experimental observation. Furthermore, the fact that there is no change observed in the spectrum between the first and the second intermediate indicates that both intermediates have very similar spectra in the UV–vis range. Thus, $[Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+}$ – Intermediate I is undergoing a chemical conversion to produce a second intermediate: Intermediate II (with a very similar UV–vis spectrum as no absorption change is observed spectroscopically) $([Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+})'$ – and this second intermediate, which is more stable, undergoes a first-order intramolecular electron transfer step followed by fast hydrolysis of the divalent labile cobalt (II) and protonation of the ammine ligands to produce the final stable products:

$$\underset{\text{Intermediate II}}{([Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+})'} \rightarrow \text{products} \qquad (10a)$$

A reasonable assumption is that the first intramolecular step, reaction (11), is an isomerization reaction of the intermediate. Such a reaction might be accompanied by only minor changes in its absorption spectrum as is observed experimentally.

The final products have been determined using steady-state irradiations (20 min in the ^{60}Co γ source), of N_2O saturated solutions containing $[Co(NH_3)_5CN]^{2+}$ 1.0×10^{-3} M at the pH range 3–6 (addition of phosphate buffer 0.050 M) and 1.0 M of the appropriate alcohol, and found to be (for all three reacting α-hydroxyalkyl radicals) $G(Co^{2+}{}_{aq}) = 6.0 \pm 0.9$. In the case of the $^{\bullet}CH_2OH$ radicals, formaldehyde was determined to be the second final product with the same yield: $G = 6.0 \pm 0.6$. Thus, the yields of the final products equal those of the α-hydroxyalkyl radicals formed by the irradiation. This corroborates the suggestion that the decomposition reaction of the second intermediate is

$$\underset{\text{(Intermediate II)}}{([Co^{III}(NH_3)_5CN, {}^{\bullet}CR^1R^2(OH)]^{2+})'}$$
$$\xrightarrow{5H^+} Co^{2+}{}_{aq} + CR^1R^2 = O + 5NH_4{}^+ \qquad (12)$$

3.3. Reactivity of $[Co(NH_3)_5CN]^{2+}$ with other aliphatic radicals

It was decided to try and check the reactivity of the trivalent cobalt pentaamminecyano complex with other aliphatic radicals. For this purpose, N_2O saturated solutions containing $(1\text{–}10) \times 10^{-4}$ M $[Co(NH_3)_5CN]^{2+}$ at pH 3–6 (phosphate buffer 0.050 M) and 0.50 M *tert*-butanol or 0.30 M of DMSO (dimethyl sulfoxide) or 0.10 M glycolic acid, or 0.050 M sodium formate or 0.10 M ethylene glycol were irradiated in the linear accelerator. The corresponding radicals have been produced: $^{\bullet}CH_2C(CH_3)_2OH$, $^{\bullet}CH_3$, $^{\bullet}CH(OH)CO_2{}^-$, $^{\bullet}CH_2CHO$ and $^{\bullet}CO_2{}^-$. When the solution containing DMSO was saturated with $80\%N_2O/20\%O_2$, the $CH_3O^{\cdot}{}_2$ radical is the reacting species produced. For all these radicals, no intermediates were observed. No effect of the $[Co(NH_3)_5CN]^{2+}$ complex concentration on the kinetics of disappearance of the radicals was observed. The reactions obeyed second-order rate laws corresponding to the bimolecular radical reaction (9).

For the methyl radicals the yield of ethane and methane which are the gaseous products from methyl radical reactions via reaction (9) and via hydrogen atom abstraction from DMSO, was the same in the presence and absence of the $[Co(NH_3)_5CN]^{2+}$ complex. Furthermore, when identical solutions were irradiated in a ^{60}Co γ-source, no $Co^{2+}{}_{aq}$ was formed as a final product. These observations indicate that these aliphatic radicals do not react (or have low reactivity, $k < 1.5 \times 10^6\ M^{-1}\ s^{-1}$) with the cobalt (III) pentaamminecyano complex. As the attack of the α hydroxyaliphatic radicals is shown to be on the cyano ligand, this observation suggests that these radicals have an increased reactivity towards the cyano group. Furthermore, the fact that no $Co^{2+}{}_{aq}$ was formed indicates that the ammine ligands are not susceptible to an attack by the aliphatic radicals or for electron transfer step to the central trivalent cobalt via the outer sphere mechanism.

3.4. Nature of the intermediates observed

The short lifetime of the intermediates inhibits use of other analytical tools to determine the nature of the intermediates. It is suggested that the first intermediate formed is [A] and not [B]. This suggestion is based on the following argument: steric hindrance is expected to inhibit fast reactions of the radicals with the carbon atom of the cyano ligand.

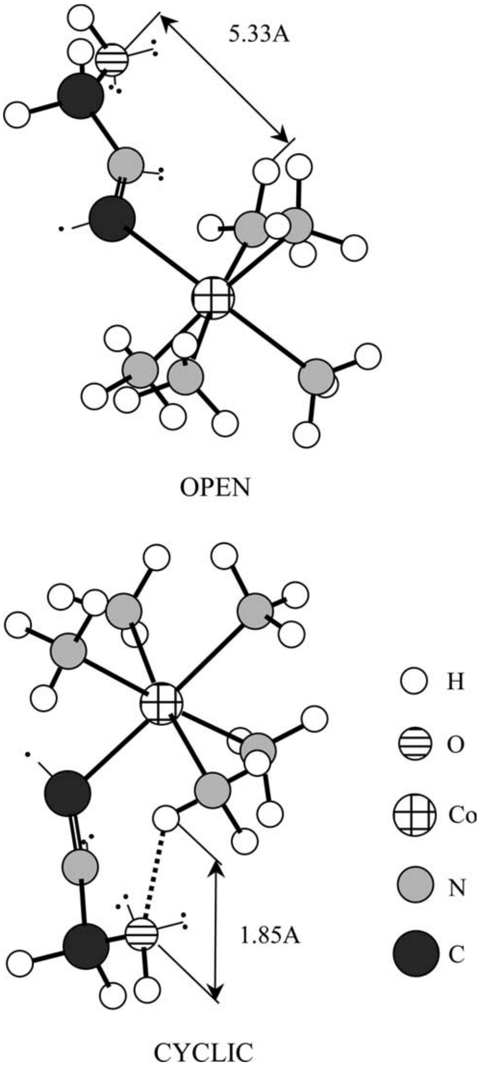


Fig. 4. Two possible configurations for the intermediate and its isomer.

The product of the isomerization reaction (11) is expected to be similar to the first transient. Theoretical calculations using the semi empirical MM2 [19] program offer such a transient couple. The calculations resemble the behavior of water by using continuous phase with the dielectric constant of water. The calculations lead to two similar transients, Fig. 4, with a small energy difference.

The first intermediate is the "OPEN INTERMEDIATE" and the isomerization product of this intermediate is the "CYCLIC INTERMEDIATE", which is more stable by ca. 4.9 kcal/mol.

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