important if the nonradiative pathways determine the lifetimes of the $^3\pi\pi^*$ sublevels. Since there are insignificant changes in the spectrum of the lowest lying $^3\pi\pi^*$ state obtained with different axial ligands, the second alternative, namely, differences in the rate constants for nonradiative relaxation, seems to provide a better description of the observed behavior.[34-38]

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2358 from the Notre Dame Radiation Laboratory. We thank Dr. D. Prasad for preparing the ruthenium(II) phthalocyanine.

Registry No. Rh(pc)(CH_3OH)Cl, 81725-25-9; Rh(pc)(CH_3OH)Br, 81725-26-0; Rh(pc)(CH_3OH)I, 81725-27-1; Al(pc)Cl, 14154-42-8; $[Co(pts)]^{3-}$, 69087-63-4; $[Cu(pts)]^{4-}$, 67462-31-1; Ru(pc)$(py)_2$, 67588-46-9.

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[38] J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, **18**, 1589 (1965).

[39] Notice that the temperature dependence of the rate constant is in agreement with the behavior expected for a weak-coupling mechansm.[36,40]

[40] W. Siebrand in "The Triplet State", Beirut Symposium, A. B. Zahlan, Ed., Cambridge University Press, London, 1967.

Contribution from the Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel,
Nuclear Research Centre Negev, Beer-Sheva, Israel, and Kent State University, Kent, Ohio 44242

Intermolecular vs. Intramolecular Reduction of Cobalt(III) Centers by Coordinated Pyridinyl Radicals

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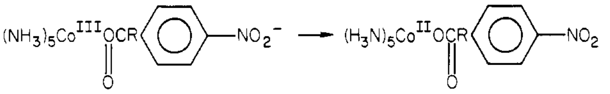
Received July 9, 1982

Four pentaamminecobalt(III) complexes, bound via a nonconjugated carboxylate to a pyridinyl derivative, were reduced by aliphatic free radicals. The primary site of reduction is shown to be the pyridinyl group. In one of the complexes studied an intramolecular electron transfer from the free radical to the cobalt center is observed, $k_{IET} = 4 \times 10^4\ s^{-1}$. Surprisingly the coordinated pyridinyl radicals in the other complexes reduce another cobalt(III) center via an intermolecular process. The origin of the different patterns of behavior is discussed.

Introduction

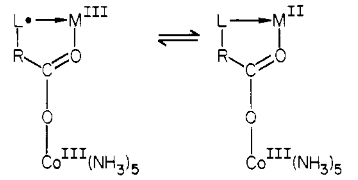
Our interest in the factors affecting the rate of intramolecular electron-transfer reactions prompted us to study the effect of "interrupted conjugation" on the rate of reduction of pentaamminecobalt(III) centers by pyridinyl radicals bound to the cobalt by an insulated carboxylate group. While this study was in progress, Hoffman et al. reported[2] results on the analogous reactions



(1)

Their results suggested that the rate of reaction 1 depends only slightly on the nature of –R– for R = CH_2, CH=CH, and $(CH_2)_3$.

The choice of complexes studied stemmed also from the suggestion[3] that the mechanism of reduction of $(NH_3)_5CoOC(O)RL$ by Eu^{2+} and Cr^{2+} involves intermediates of the type



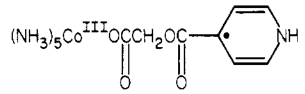
(2)

It seemed thus of interest to study the rates of the reaction

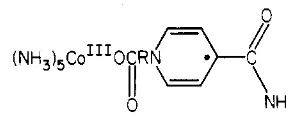
$$(NH_3)_5Co^{III}OC(O)RL^{-}\cdot \rightarrow (NH_3)_5Co^{II}OC(O)RL \quad (3)$$

Furthermore the ligands ^-O_2CRL were shown[4] to be catalysts for the reduction of cobalt(III) complexes by Eu^{2+}.

We report here the surprising result that we observed an intramolecular electron transfer only for the complex



whereas for complexes of the type

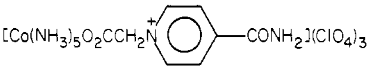


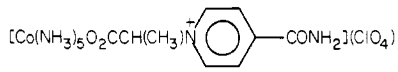
we observed intermolecular redox reactions of the type

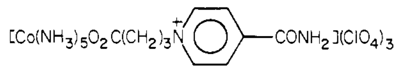
$$(NH_3)_5Co^{III}OC(O)RL^{-}\cdot + (NH_3)_5Co^{III}OC(O)RL \rightarrow (NH_3)_5Co^{III}OC(O)RL + (NH_3)_5Co^{II}OC(O)RL \quad (4)$$

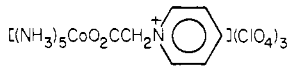
Experimental Section

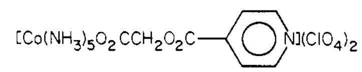
Materials. The complexes











were prepared according to procedures described in the literature.[5]

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[1] (a) Nuclear Research Centre Negev. (b) Kent State University. (c) Ben-Gurion University of the Negev.

[2] Whitborn, K. D.; Hoffman, M. Z.; Simic, M. G.; Brezniak, N. V. *Inorg. Chem.* **1980**, *19*, 3180.

[3] (a) Srinivasan, V. S.; Radlowsky, C. A.; Gould, E. S. *Inorg. Chem.* **1981**, *20*, 2094. (b) Srinivasan, V. S.; Radlowsky, C. A.; Gould, E. S. *Ibid.* **1981**, *20*, 3172. (c) Where "L" is a γ-activated pyridine ring.

[4] (a) Norris, C.; Nordmeyer, F. R. *J. Am. Chem. Soc.* **1971**, *93*, 4044. (b) Dockal, E. R.; Gould, E. S. *Ibid.* **1972**, *94*, 6673. (c) Chen, J. C.; Gould, E. S. *Ibid.* **1973**, *95*, 5539. (d) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Heh J. C.-K.; Gould, E. S. *Inorg. Chem.* **1977**, *16*, 1942. (e) Fanchiang, Y.-T.; Gould, E. S. *Ibid.* **1978**, *17*, 1827.

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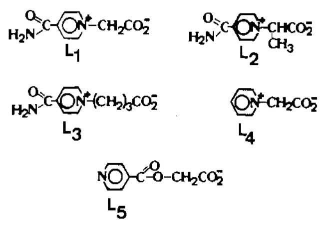

Figure 1. Structures of the ligands investigated L_{1-5}.

All other chemicals used were of analytical grade and were used without further purification. Water, deionized by using a Milli-Q Millipore setup, with a resistance $\geq 10^7$ Ω/cm was used throughout this study. The pH was adjusted with $HClO_4$ and NaOH. Nitrous oxide was purified from dioxygen traces by bubbling through a train of washing bottles containing VSO_4 in dilute H_2SO_4 over zinc amalgam, followed by a washing bottle containing pure water.

Notation. The structures of the different ligands L_1–L_5 are given in Figure 1. In order to simplify the notation of the complexes, Co^{III} will be used instead of $Co^{III}(NH_3)_5$, and $Co^{III}Li$, instead of $Co^{III}(NH_3)_5Li$.

Irradiations. The pulse radiolytic experiments were carried out with use of 0.05–1.5-μs, 5-MeV, 200-mA pulses from the electron linear accelerator at the Hebrew University of Jerusalem. The dose per pulse was 150–3000 rd. The experimental setup and the methods used for evaluating the results have been described elsewhere in detail.[6a]

Kinetics. Solutions were saturated with N_2O or Ar before irradiations. The kinetics of appearance or bleaching of absorbance were followed. Pseudo-first- or second-order rates were calculated when the appropriate logarithmic or reciprocal plot was linear for at least 3 half-lives. All experiments were carried out at room temperature, 22 ± 2 °C.

Production of Reducing Reagents.[6b] The radiolysis of water by ionizing radiation can be described by eq 5.[7]

$$H_2O \xrightarrow{\gamma,\, e^-} e_{aq}^-, OH, H, H_2O_2, H_2, H_3O^+ \qquad (5)$$

The yields of the products are $G(e_{aq}^-) = 2.65$, $G(OH) = 2.65$, $G(H)$, $= 0.60$, $G(H_2) = 0.45$, and $G(H_2O_2) = 0.75$ (where the G value is the number of product molecules formed by the absorption of 100 eV in the solution). Somewhat higher yields are expected in concentrated solutions.[7] The products are homogeneously distributed within less than 10^{-7} s after the absorption of the radiation.

a. Reactions with e_{aq}^-. In 0.1 M *tert*-butyl alcohol solutions saturated with Ar, the following reaction occurs:

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH + H_2O \qquad k = 5.2 \times 10^8\ M^{-1}\ s^{-1} \qquad (6)$$

and as the $\cdot CH_2C(CH_3)_2OH$ radical is a weak reducing agent that does not react with amminecobalt(III) complexes,[8] the main reactive species remaining in solution within less than 1 μs after the pulse is the hydrated electron.

b. Production of $(CH_3)_2\dot{C}OH$ or $CO_2^-\cdot$ Radicals. In 0.1 M 2-propanol or 0.1 M sodium formate solutions saturated with N_2O (~2 × 10^{-2} M), the following reactions occur:

$$e_{aq}^- + N_2O \rightarrow N_2 + OH \qquad k_8 = 8.7 \times 10^9\ M^{-1}\ s^{-1} \qquad (7)$$

$$e_{aq}^- + H_3O^+ \rightarrow \cdot H + H_2O \qquad k_9 = 2.3 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (8)$$

$$(CH_3)_2CHOH + OH/H \rightarrow (CH_3)_2\dot{C}OH + H_2O/H_2 \qquad (9a)$$

$$k_{OH} = 2 \times 10^9\ M^{-1}\ s^{-1} \qquad k_H = 7.5 \times 10^7\ M^{-1}\ s^{-1} \qquad (9b)$$

$$HCO_2^- + OH/H \rightarrow CO_2^-\cdot + H_2O/H_2 \qquad (10a)$$

$$k_{OH} = 3.0 \times 10^9\ M^{-1}\ s^{-1} \qquad k_H = 1.8 \times 10^8\ M^{-1}\ s^{-1} \qquad (10b)$$

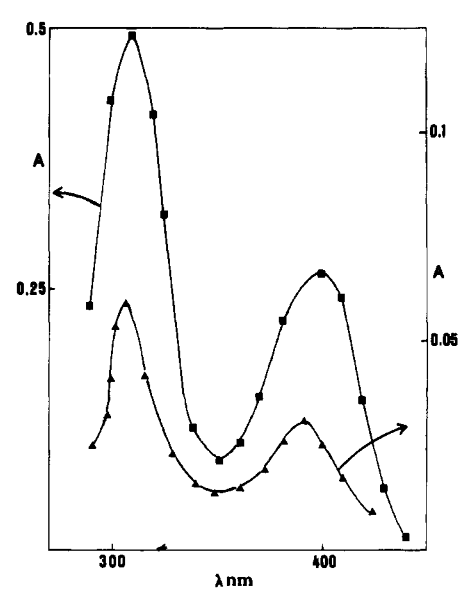

Figure 2. Absorption spectra of the transients formed via the reaction of (■) formate radicals $CO_2^-\cdot$ with L_5 to form $L_5^-\cdot$ in solutions containing 0.1 M HCO_2Na and 2 × 10^{-4} M L_5 at pH 5.5 saturated with N_2O (pulse intensity 1000 rd) and (△) the hydrated electron with $(NH_3)_5Co^{III}L_5$ to form $(NH_3)_5Co^{III}L_5^-\cdot$ in solutions containing 0.1 M *tert*-butyl alcohol and 4 × 10^{-5} M $(NH_3)_5Co^{III}L_5$ saturated with Ar (pulse intensity 1000 rd). The absolute absorption coefficients were determined in N_2O-saturated solutions containing 0.1 M HCO_2Na and 2 × 10^{-4} M complex.

Thus, the only reactive species within 1 μs after the pulse are the $(CH_3)_2\dot{C}OH$[9] or the $CO_2^-\cdot$ radicals (depending on the organic solute added).

c. Production of Ni^+ and Cd^+. Monovalent nickel and cadmium cations were produced in solution by irradiations of Ar-saturated solutions containing 1 M *tert*-butyl alcohol and 0.1 M $NiSO_4$ or $CdSO_4$, respectively. The following reactions occur:

$$e_{aq}^- + Ni^{2+}/Cd^{2+} \rightarrow Ni^+/Cd^+ \qquad (11)$$

$$OH + (CH_3)_3COH \rightarrow \cdot CH_2C(CH_3)_2OH \qquad (12)$$

$\cdot CH_2C(CH_3)_2OH$ radicals react[10] with Ni^+/Cd^+ but in the presence of high concentrations of oxidants, e.g., $Co^{III}L$ complexes; the reactions of $Cd^+(aq)/Ni^+(aq)$ with these oxidants can be studied.

Results and Discussion

Noncoordinated Pyridinyl Free Radicals. Argon and nitrous oxide saturated neutral solutions containing 0.1 M HCO_2Na or 1 M 2-propanol and the free ligands L_1, L_3, L_4, and L_5 were irradiated. (We had no sample of L_2.) In argon-saturated solutions L_1, L_3, and L_5 react with the two reducing radicals $CO_2^-\cdot$ and $\cdot C(CH_3)_2OH$ to yield the same intermediate. The spectral properties of the transients in the three systems are similar to each other and to other pyridinyl radicals reported in the literature.[13] We therefore assume that the reactions observed are (13) and (14). The spectral properties of the free radicals, $L^-\cdot$, are summarized in Table I, and a typical

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(5) Radlowski, C. A.; Gould, E. S. *Inorg. Chem.* **1979**, *18*, 1289.

(6) (a) Cohen, H.; Nutkovich, M.; Wieghardt, K.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1982**, 943. (b) Specific rates of reaction were taken from: Bambeneck, M.; Ross, A. B. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) **1973**, *NSRDS-NBS 43*. Anbar, M.; Farhataziz; Ross, A. B. *Ibid.* **1975**, *NSRDS-NBS 51*. Farhataziz; Ross, A. B. *Ibid.* **1977**, *NSRDS-NBS 59*.

(7) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969.

(8) Cohen, H.; Meyerstein, D. *J. Am. Chem. Soc.* **1972**, *94*, 6944.

(9) Ca. 14% of the $\cdot CH_2CH(OH)CH_3$ radicals are formed in the reaction of OH radicals with isopropyl alcohol.[10] However, these radicals are weak reducing agents like $\cdot CH_2C(CH_3)_2OH$ and do not intervene in reactions.

(10) Asmus, K. D.; Hockal, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

(11) These low-valent cations are known[12] to react with $\cdot CH_2C(CH_3)_2OH$ radicals to yield $M^{II}CH_2C(CH_3)_2OH$, but these are second-order reactions. In the presence of high enough concentrations of the oxidants, the reduction of the latter by $M^+(aq)$ can be studied.

(12) (a) Kelm, M.; Lilie, J.; Henglein, A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1132. (b) Kelm, M.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1974**, *78*, 882.

(13) (a) Kosower, E. M. "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976. (b) Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4808.

Table I. Spectral Data of Free and Coordinated Pyridinyl Radicals[a]

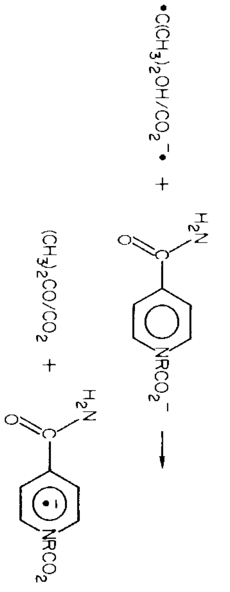
	L_1		L_2		L_3		L_5	
	λ_1 (ϵ_1)	λ_2 (ϵ_2)	λ_1 (ϵ_1)	λ_2 (ϵ_2)	λ_1 (ϵ_1)	λ_2 (ϵ_2)	λ_1 (ϵ_1)	λ_2 (ϵ_2)
L	313 (1.2×10^4)	410 (8.3×10^3)	*b*	*b*	310 (1.7×10^4)[c]	400 (1.2×10^4)[c]	313 (1.35×10^4)	397 (8.7×10^3)
RoL	310 (8.0×10^2)	410 (4.0×10^2)	310 (8.0×10^2)[d]	400 (3.7×10^2)[d]	315 (6.5×10^2)	400 (3.0×10^2)	308 (8.0×10^2)	393 (4.0×10^2)
RoLH	313 (3.2×10^3)	412 (2.0×10^3)	320 (1.0×10^3)	415 (5.0×10^2)	320 (1.65×10^3)	413 (1.2×10^3)	315 (1.7×10^3)	400 (1.1×10^3)

[a] The protonated forms were obtained at pH 1, and the deprotonated forms, in the range pH 4.5–6.0. For further details, see the Experimental Section. Values of wavelengths maxima are given in nm, and those of the molar absorption coefficients, in M^{-1} cm^{-1}. [b] No data measured due to lack of the ligand. [c] The reducing radical was $CO_2^-\cdot$ and not $\cdot C(CH_3)_2OH$. [d] Lower limits because of interference of the decay reaction of the coordinated pyridinyl radicals.

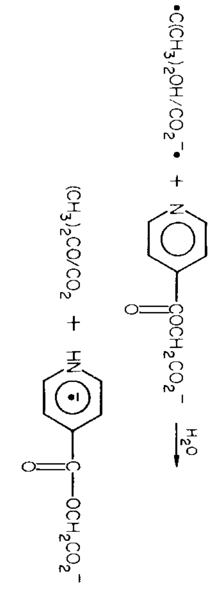
Table II. Specific Rate of Reduction of Free and Coordinated Pyridines by $\cdot C(CH_3)_2OH$ Radicals and of Hexaamminecobalt(III) by $L^-\cdot$/LH· Radicals[a]

	L_1	L_2	L_3	L_5
$k_{C(CH_3)_2OH+L}$, M^{-1} s^{-1}	4.1×10^9	*c*	2.6×10^9	1.3×10^9
$k_{C(CH_3)_2OH+L}$,[b] M^{-1} s^{-1}	3.5×10^9	*c*	3.7×10^9	2.6×10^9
$k_{C(CH_3)_2OH+RoL}$, M^{-1} s^{-1}	1.6×10^{10}	$\leq 2.8 \times 10^8$ [d]	2.8×10^9	2.9×10^9
$k_{C(CH_3)_2OH+RoL}$,[b] M^{-1} s^{-1}	4.2×10^9	4.5×10^9	4.0×10^9	3.0×10^9
$k_{L^-+Co(NH_3)_6^{3+}}$, M^{-1} s^{-1}	1.1×10^8	*c*	1×10^8	4.5×10^7
$k_{LH+Co(NH_3)_6^{3+}}$,[b] M^{-1} s^{-1}	2.4×10^6	*c*	1.9×10^6	2.1×10^6

[a] The concentration of the pyridinyls was in the range (2–40) $\times 10^{-5}$ M. For further details see Experimental Section. Unless otherwise stated, the pH was in the range 4.5–5.5. [b] Measured at pH 1. [c] Ligand not available. [d] Upper limit due to completion of the decay reaction of the coordinated radical.



(13)



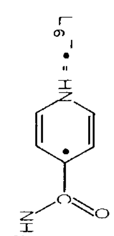
(14)

spectrum is plotted in Figure 2. In solutions containing L_3 the same transient, $L_3^-\cdot$, is observed also in N_2O-saturated solutions. However, the free radicals $L_1^-\cdot$ and $L_5^-\cdot$ react with N_2O. ($k_{L_1^-\cdot+N_2O} = 4.0 \times 10^6$ M^{-1} s^{-1} at pH 5.5 and $k_{L_5^-\cdot+N_2O} = 2.9 \times 10^6$ M^{-1} s^{-1} at pH 5.8.) The rates of reaction of $\cdot C(CH_3)_2OH$ with the uncoordinated ligands are summarized in Table II.

The mechanism and kinetics of decomposition of the free radicals, $L^-\cdot$, were not studied in detail. For all of them $t_{1/2}$(decomposition) > 10 ms under the experimental conditions was observed. When $Co(NH_3)_6^{3+}$ is added to the solutions, the rate of disappearance of the absorption due to $L^-\cdot$ is enhanced, and the processes obey first-order rate laws. Thus the specific rates of reaction 15 were measured. The rates are summarized in Table II. The rate of reaction 15 for all three

$$L^-\cdot + Co(NH_3)_6^{3+} \rightarrow L + Co(NH_3)_6^{2+} \qquad (15)$$

free radicals, $L^-\cdot$, is considerably higher than that reported for

$L_6^-\cdot$ =


suggesting that the redox potential for the couples $L_i/L_i^-\cdot$ (i = 1, 3, 5) is more negative than that of $L_6/L_6^-\cdot$ for which $E°$ = −0.80 V.[14] The same experiments were carried out at pH 1.0 in solutions containing $CH(CH_3)_2OH$, and similar results were obtained. However, the spectra of the transients are slightly different, and the rates measured for reaction 15 are considerably lower. These results suggest that the $L^-\cdot$ radicals have a p*K* yielding LH· radicals in acidic solutions, in agreement with expectations.

The free ligand L_4 does not react, under the experimental conditions, with $\cdot C(CH_3)_2OH$, CO_2^-, Cd^+(aq), and Ni^+(aq). This observation is in agreement with expectations as electron-withdrawing groups facilitate the reduction of pyridines.[13]

Reduction of $(H_3N)_5Co^{III}L$ Complexes. The complexes $(NH_3)_5Co^{III}L_i$, i = 1, 2, 3, 5, react with $\cdot C(CH_3)_2OH$ and $CO_2^-\cdot$ to yield short-lived transients with spectra independent of the reducing radical. The rates of reaction of $\cdot C(CH_3)_2OH$ with the complexes are summarized in Table II.

The spectral data regarding these short-lived intermediates are summarized in Table I, and a typical spectrum is shown in Figure 2. It is clear from the results that the spectra of the free radicals $Li^-\cdot$ are similar to those of the transients obtained in the reduction of $(NH_3)_5Co^{III}Li$. However, we note that the molar absorption coefficients in the latter case are ca. 1 order of magnitude smaller. The specific rates of reaction of the $\cdot C(CH_3)_2OH$ free radicals with $(NH_3)_5Co^{III}Li$ are similar to those with Li (Table II) and are considerably higher than the

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(14) Cohen, H.; Meyerstein, D. *Isr. J. Chem.* **1974**, *12*, 1049.

Table III. Specific Rate of Intermolecular vs. Intramolecular Reduction of Co^{III} Centers by Coordinated Pyridinyl Radicals[a]

	L_1	L_2	L_3	L_5
k_{RoL^-+RoL}, $M^{-1}\ s^{-1}$	1.5×10^9	1.4×10^9	1.0×10^8	$\leqslant 1 \times 10^7$
$k_{RoLH\cdot+RoL}$,[b] $M^{-1}\ s^{-1}$	1.6×10^8	1.5×10^8	3.0×10^7	$\leqslant 6 \times 10^6$
k_{IET}, s^{-1}	$\leqslant 2 \times 10^4$	$\leqslant 2 \times 10^4$	$\leqslant 2 \times 10^4$	4.0×10^4
k_{IET},[b] s^{-1}	$\leqslant 1 \times 10^4$	$\leqslant 1 \times 10^4$	$\leqslant 1 \times 10^4$	2.0×10^4

[a] The concentrations of the RoL complexes in the solution were in the range $(5-30) \times 10^{-5}$ M. The pH of the solutions was in the range 4.5-5.5, unless otherwise stated. [b] The pH of the solutions was 1.0.

rate of the reaction $\cdot C(CH_3)_2OH + Co(NH_3)_6^{3+} \rightarrow C(CH_3)_2O + H_3O^+ + Co(NH_3)_6^{2+}$ ($k = 1.3 \times 10^7\ M^{-1}\ s^{-1}$) at pH 6.0.[15] We conclude therefore that the reactions of the free radicals $CO_2^-\cdot$ and $\cdot C(CH_3)_2OH$ with $(NH_3)_5Co^{III}L_i$ result in the production of the short-lived intermediates $(NH_3)_5Co^{III}L_i^-\cdot$ via reaction 16.[16,18]

$$CO_2^-\cdot/\cdot C(CH_3)_2OH + (NH_3)_5Co^{III}L_i \rightarrow CO_2/(C(CH_3)_2O + H_3O^+) + (NH_3)_5Co^{III}L_i^-\cdot \quad (16)$$

Mechanism of Decomposition of $(NH_3)_5Co^{III}L^-\cdot$. The mechanism of decomposition of all reducing free radicals ligated to cobalt(III) studied so far involved one of the reactions

$$Co^{III}L^-\cdot \xrightarrow{IET} Co^{II}L \quad (17)$$

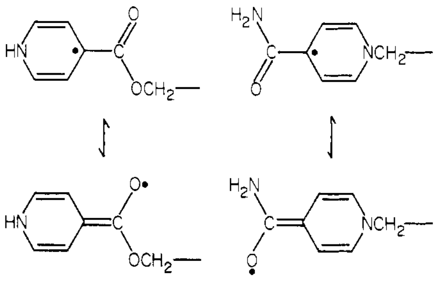
$$2Co^{III}L^-\cdot \xrightarrow{2H^+} Co^{III}L + Co^{III}LH_2 \text{ (or } Co^{III}LLCo^{III}) \quad (18)$$

(where LH_2 represents L reduced by two electrons). In the present study we observed that indeed the decomposition of $(NH_3)_5Co^{III}L_i^-\cdot$ obeys a pseudo-first-order rate law, the rate being independent of the wave length or pulse intensity, for i = 1, 2, 3, and 5. However, only for i = 5 was the observed rate of reaction independent of $[(NH_3)_5Co^{III}L_5^{2+}]$ as expected for decomposition via the IET mechanism. For i = 1, 2, and 3, surprisingly enough, the observed rate of reaction depends linearly on $[(NH_3)_5Co^{III}L_i^{3+}]$. This result indicates that the reaction observed here is

$$(NH_3)_5{}^*Co^{III}L_i^-\cdot + (NH_3)_5Co^{III}L_i \rightarrow (NH_3)_5{}^*Co^{III}L_i + (NH_3)_5Co^{II}L_i \quad (19)$$

(where the * is used only for distinction between the two complexes in the equation). Thus the results (Table III) show that reaction 19 must be considered as an additional mechanism for the catalysis of reduction of cobalt(III) complexes.

The observation that the rates of reduction of $Co(NH_3)_6^{3+}$ by $L_1^-\cdot$, $L_3^-\cdot$, and $L_5^-\cdot$ are similar (Table II) suggests that the redox potentials of these free radicals are similar. We suggest that the difference between the mechanism of reaction of $(NH_3)_5Co^{III}L_{1,2,3}^-\cdot$ and $(NH_3)_5Co^{III}L_5^-\cdot$ stems from the fact that in the latter complex the unpaired electron is expected to be located nearer the cobalt center than for the other complexes,[19] as can be deduced from the major contributing resonance structures.[13,21]



$L_5^-\cdot$ $L_{1,2,3}^-\cdot$

We note that the rate of the intermolecular electron transfer is slower for $(NH_3)_5Co^{III}L_5H\cdot$, as expected (Table III).[23]

Finally, we wish to point out that the shift from the intramolecular to the intermolecular electron-transfer mechanism probably involves only small changes in the activation energy of the two processes if their rates are similar. Thus, from the observed rates of reaction upper limits for the rate of reaction via the unobserved mechanism can be calculated. These upper limits are included in Table III and indicate that a change of >2 kcal/mol in ΔG^* can cause the change in the predominant mechanisms observed.

Registry No. $[(NH_3)_5Co^{III}(L_5)]^{2+}$, 77482-17-8; $[(NH_3)_5Co^{III}(L_1)]^{3+}$, 69421-18-7; $[(NH_3)_5Co^{III}(L_2)]^{3+}$, 69421-20-1; $[(NH_3)_5Co^{III}(L_3)]^{3+}$, 69421-22-3; L_1, 72121-35-8; L_3, 84896-19-5; L_5, 84896-20-8; $CO_2^-\cdot$, 14485-07-5; $\cdot C(CH_3)_2OH$, 5723-74-0; $L_1^-\cdot$, 85027-92-5; $L_3^-\cdot$, 85027-93-6; $L_5^-\cdot$, 85027-91-4; $Co(NH_3)_6^{3+}$, 14695-95-5.

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(15) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1056.

(16) The source of the difference in the molar absorption coefficients between $L^-\cdot$ (or $LH\cdot$) and $(NH_3)_3Co^{III}L^-\cdot$ is not clear. The rates of reaction of $\cdot C(CH_3)_2OH$ with the complexes suggest that the source of the difference is not a decrease in their yields. Thus the results suggest that ligation causes a change in the transition probability nearly without affecting the energy of the electonic levels involved. This conclusion is surprising as in analogous systems ligation has little effect on the transition probabilities.[6a,17]

(17) (a) Neta, P.; Simic, M. G.; Hoffman, M. Z. *J. Phys. Chem.* **1976**, *80*, 2018. (b) Wieghardt, K.; Cohen, H.; Meyerstein, D. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 388.

(18) The results cannot be explained by the sequence

$$Co^{III}L + CO_2^-\cdot \rightarrow Co^{III}\text{–}L^-\cdot \xrightarrow{fast} Co^{II}\text{–}L \xrightarrow{fast} Co^{II} + L \xrightarrow{+CO_2^-\cdot} Co^{II} + L^-\cdot$$

due to the following arguments: (a) A small absorption coefficient is observed also for $Co^{III}\text{–}L_5^-\cdot$, and as here we observe an intramolecular electron-transfer process, clearly $L_5^-\cdot$ is bound to the cobalt. (b) There seems to be no reason that the rate of IET is orders of magnitude faster for $Co^{III}L_{1,2,3}^-\cdot$ than for $Co^{III}L_5^-\cdot$. (c) If this sequence would occur, then one would expect an apparent larger absorption coefficient when lower concentrations of $Co^{III}L_i$ are used; the opposite is observed.

(19) The distance through which the electron has to tunnel is expected to increase considerably the activation energy for the IET process.[20]

(20) Oliviera, L. A. A.; Haim, A. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; American Chemical Society: Washington, D.C., 1982; INOR 235.

(21) EPR studies[22] on 4-substituted pyridines indicate that the highest spin density is on the oxygen of the carbonyl of the substituent on the 4- and 2-carbon atoms, and on the ring nitrogen.

(22) Neta, P.; Patterson, L. K. *J. Phys. Chem.* **1974**, *78*, 2211.

(23) One of the reviewers suggested that the enolic form $NC_5H_4C(O)\text{-}OCH{=}C(OH)ORo$ is more easily attained in L_5 than in L_1 and L_2 and that this is the major source for the difference is reactivity.