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# Reaction Mechanism of Cobalt(III)–Polyamine Complexes with OH Radicals

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The reactions of the cobalt(III)–polyamine complexes $[Co(en)_3]^{3+}$, $[Co(dien)_2]^{3+}$, $[CoCl_2(en)_2]^+$, and $[CoCl_2(trien)]^+$ (en = ethylenediamine, dien = diethylenetriamine, trien = triethylenetetramine) with OH radicals have been investigated by conductometric pulse radiolysis in weak acid solutions. All complexes react with OH with $k = (3.0 \pm 0.2) \times 10^8\ M^{-1}\ s^{-1}$. The ligands are oxidized and the Co(III) is reduced to Co(II) by the oxidized ligands. The dissociation rates of the degraded and undegraded ligands are measured, and the rate constants for all complexes examined are shown to increase with increasing hydrogen ion concentration. The primary oxidation mechanisms of these complexes are discussed.

## Introduction

In previous papers[1,2] we have shown that Co(III) complexes are reduced to the Co(II) state by hydrated electrons that are produced by the radiolysis of water. The ligands of the reduced complexes dissociate stepwise with pH-dependent rates. For the complex with ethylenediamine ligands (en) the reactions are (coordinated water is neglected) (1)–(4).

$$[Co(en)_3]^{3+} + e_{aq}^- \rightarrow [Co(en)_3]^{2+} \qquad (1)$$
$$k = 8.2 \times 10^{10}\ M^{-1}\ s^{-1}$$

$$[Co(en)_3]^{2+} + 2H^+ \rightarrow [Co(en)_2]^{2+} + enH_2^{2+} \qquad (2)$$

$$[Co(en)_2]^{2+} + 2H^+ \rightarrow [Co(en)]^{2+} + enH_2^{2+} \qquad (3)$$

$$[Co(en)]^{2+} + 2H^+ \rightarrow Co^{2+} + enH_2^{2+} \qquad (4)$$

The question arises as to which mechanisms take place when the complexes are oxidized. In the radiolysis of aqueous solutions one of the major radicals formed is OH, a powerful oxidizing agent. As the OH radical and the short-lived intermediates formed by its reaction with cobalt–polyamine complexes are very poor at absorbing light, those measurements are only possible by conductometric pulse radiolysis, and optical detection systems cannot be used to determine those mechanisms.

The reaction mechanisms of the oxidation of cobalt–polyamine complexes are of interest because it has been found that metal ions catalyze the oxidative dehydrogenation of coordinated amines to imines. It was indicated that the net reaction involved prior oxidation of the metal center followed by an oxidation of the ligand and the reduction of the metal center.[4–10]

Ruthenium(II)–ethylenediamine complexes undergo oxidation chemically and electrochemically, and the reactions result in oxidative dehydrogenation of ethylenediamine to give an imine complex.[4–10] In the radiolytic oxidation of copper(II)- and nickel(II)–ethylenediamine complexes, the oxidative dehydrogenation of ethylenediamine is initiated by the oxidation of M(II) to M(III)[11–13] and subsequent ligand oxidation.

## Experimental Section

$[Co(en)_3]Br_3$,[14] *trans*-$[CoCl_2(en)_2]ClO_4$,[15] $[Co(dien)_2](ClO_4)_3$,[16] and *cis*-$[CoCl_2(trien)]ClO_4$[17] were prepared according to the literature and $[Co(en)_3]Br_3$ was changed to the perchlorate salt with silver perchlorate.

For the measurements of the ligand-dissociation kinetics $N_2O$-saturated aqueous solutions with $5 \times 10^{-4}$ M cobalt(III)–polyamine complex were prepared. pH values of 2.9–4.5 were achieved by adjustment with $HClO_4$. To minimize the effect of hydrolysis of $[CoCl_3(en)_2]^+$ and $[CoCl_2(trien)]^+$, we saturated solutions with $N_2O$ before addition of the complexes and the measurements were carried out as quickly as possible.

For the determination of the rates of OH attack on the complexes the competition method with KSCN[18] was used: in argon-purged solutions of $10^{-3}$ M cobalt(III)–polyamine complex with different concentrations of thiocyanate the absorption of the $(SCN)_2^-$ at 480 nm was measured ($\epsilon$ 7000 $M^{-1}\ cm^{-1}$). The rate constant of OH radicals with $SCN^-$ was taken as $k = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$ [18] the equilibrium

$$SCN + SCN^- \rightleftharpoons (SCN)_2^- \quad K = 2 \times 10^5\ M^{-1} \qquad (5)$$

was considered. In these competition measurements no $N_2O$ was used and the electrons could react with the Co complexes (the products of this reaction have no absorption at the wavelength observed).

Table I. Rates Constants of Cobalt(III)–Polyamine Complexes with OH Radicals

| | competitive method | | | direct obsn of conductance | |
|---|---|---|---|---|---|
| | pH | $k$, $10^8$ $M^{-1}$ $s^{-1}$ | competitor | pH | $k$, $10^8$ $M^{-1}$ $s^{-1}$ |
| $[Co(en)_3]^{3+}$ | 4.4 | 3.0 | $SCN^-$ | | |
| $[Co(dien)_2]^{3+}$ | 4.4 | 3.2 | $SCN^-$ | | |
| $[CoCl_2(en)_2]^+$ | 4.4 | 3.1 | $SCN^-$ | 2.9–4.5 | ~3.0 |
| | 6.0 | 3.2 | benzoate ion | | |
| $[CoCl_2(trien)]^+$ | 4.5 | 2.8 | $SCN^-$ | 3.0–4.5 | ~2.7 |
| $enH_2^{2+}$ | 5 | 1.0[a] | | | |

[a] Reference 21.

The pulse radiolysis equipment (1.6-MeV Van de Graaff generator, pulse duration 0.5 μs) and the 10-MHz kinetic conductivity technique have been described.[1] The dose per pulse was typically 200 rd corresponding to $10^{-6}$ mol of radicals. The measurements were carried out at room temperature (25 °C). The data obtained were analyzed on line with a PDP-11 computer.[2]

## Results and Discussion

**(a) Reaction Rates of Cobalt(III)–Polyamine Complex with OH Radicals.** It is commonly accepted that primary products of the radiolysis of aqueous solution are

$$H_2O \rightarrow e_{aq}^-,\ H,\ OH,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (6)$$

with the yields of the products in neutral solution being $G(e_{aq}^-) = 2.7$, $G(OH) = 2.7$, $G(H) = 0.6$, $G(H_2O_2) = 0.75$, and $G(H_2) = 0.45$ (the "*G* value" is defined as the number of molecules of products formed by the absorption of 100 eV by the sample). When the solution is saturated with $N_2O$ ($2 \times 10^{-2}$ M), the hydrated electrons are converted to OH according to eq 7

$$N_2O + e_{aq}^- + H^+ \rightarrow N_2 + OH \qquad (7)$$
$$k = 8.7 \times 10^9\ M^{-1}\ s^{-1}$$ [20]

which also consumes the protons formed in (6). The only reactive radiolysis products are OH radicals and the small amount of H atoms.

The reaction rates of the OH radicals with the complexes were determined by the competition with KSCN, because the products of the reaction of OH with cobalt(III)–polyamine complexes have very small absorptions ($\epsilon$ <500 $M^{-1}\ cm^{-1}$). Table I shows the measured rate constants that were calculated

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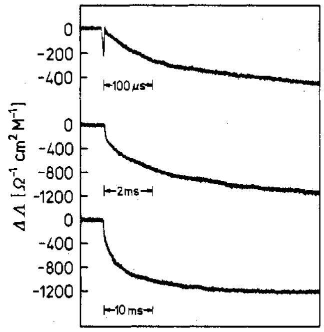


**Figure 1.** Oscilloscope traces of conductivity vs. time for the ligand dissociation after pulse irradiation of an $N_2O$-saturated $[Co(en)_3]^{3+}$ solution at pH 2.9.

from measurements with different ratios of [Co(III)–polyamine]/[KSCN]. As a check, the $[CoCl_2(en)_2]^+$ competition with benzoate ($k_{OH} = 5.7 \times 10^9$ M$^{-1}$ s$^{-1}$[18]) was also used and gave the same results.

All rate constants were found to be nearly the same in spite of the different polyamine ligands. This was found even in the complexes where two coordination positions were occupied with $Cl^-$ ions. The rate constant of a single ligand en with OH radicals has been reported to be $1.0 \times 10^8$ M$^{-1}$ s$^{-1}$ at pH 5[21] where en exists as protonated form $enH_2^{2+}$ (p$K_1$ = 7.47, p$K_2$ = 10.18[22]). Thus, cobalt(III)–polyamine complexes react with OH radicals about 3 times faster than $enH_2^{2+}$. This factor corresponds just to the higher statistical probabilities of OH attack: e.g., three en in $[Co(en)_3]^{3+}$ compared to a single ethylenediamine. It therefore can be considered as one indication that the same mechanism, i.e., H-atom abstraction, takes place in both cases.

**(b) Reaction Mechanism of $[Co(en)_3]^{3+}$ with OH Radicals.** The oscillograms (Figure 1) of an $N_2O$-saturated solution of $[Co(en)_3]^{3+}$ show no conductivity change immediately after the pulse (the small spike in the first 5 µs is a perturbation by the pulse). A decay of the conductivity that is composed of three steps then follows. Measurements at different doses showed that the rates were independent of the initial concentration of radicals; i.e., the decays always obeyed first-order rate laws. The decays became faster at lower pH values, but they were independent of the $[Co(en)_3]^{3+}$ concentration. Figure 2a shows the rate of the first step at different pH values. For comparison the rate of the first ligand dissociation of reduced $[Co(en)_3]^{2+}$ as taken from ref 2 is shown (Figure 2b). One sees that the first hydrolysis step in the oxidized complex is faster than in the reduced one. Comparison of the magnitude of this conductivity change shows that in the case of OH attack the first ligand dissociation uses up one proton ($\Delta\Lambda \approx -300$ Ω$^{-1}$ cm$^2$ mol$^{-1}$) while in the hydrolysis of reduced complexes two protons were consumed.[2]

The dissociation rates and the size of conductivity change for the second and third step were the same as have been measured for the second and third step of the hydrolysis of $[Co(en)_3]^{2+}$ formed by reaction 1.[2]

The absence of a conductivity change immediately after the attack of OH to the complex leads to the general formula in eq 8. This reaction can proceed by a H-atom abstraction from

$$[CoL]^{3+} + OH \rightarrow [CoL']^{3+} + H_2O \qquad (8)$$

the ligand or by an oxidation ($e^-$ transfer forming $OH^-$) followed by a $H^+$ elimination from the complex (this will be discussed later). The product of this reaction sequence is considered as a complex of Co(II) with still two ethylenediamine ligands (because the final hydrolysis steps are the same as in reactions 3 and 4. The degraded ligand is different: it hydrolyzes more quickly and binds only one $H^+$ when hydrolyzed.

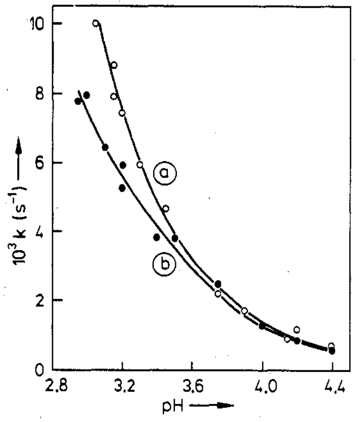
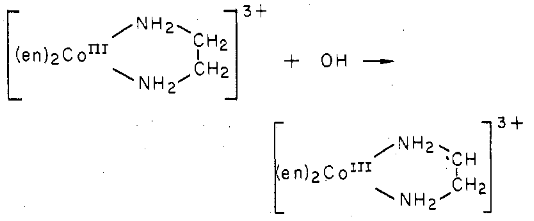


**Figure 2.** Plot of rate constants vs. pH for the dissociation of the first en for $[Co(en)_3]^{3+}$: (a) $N_2O$ saturated, (b) *tert*-butyl alcohol added (from ref 2, no $N_2O$).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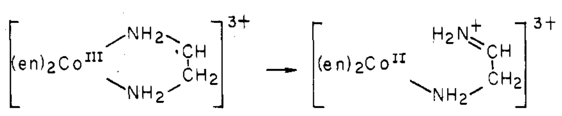

(10)

The mechanism of eq 9 and 10 explains best the observed behavior: OH radicals abstract a hydrogen from the $CH_2$ group of the ligand (reaction 9). The radical formed quickly transfers an electron to the central atom forming Co(II) and an imine group which is protonated (reaction 10). These steps proceed in the first microseconds after the pulse irradiation and cannot be separated kinetically with our apparatus.

Further evidence for the described mechanism comes from the γ radiolysis of $[Co(en)_3]^{3+}$, where Co(II) and $NH_3$ were detected: $G$(Co(II)) = 6.0, $G(NH_3)$ = 3.9–6.9 depending on pH.[23] The hydrogen abstraction from carbon and the subsequent imine formation are essential for such a deamination process. The next step in the degradation of the complex is the elimination of the monoimine ligand (eq 11). This step

$$[(en)_2Co^{II}NH_2CH_2CH{=}NH_2]^{3+} + H^+ \rightarrow [(en)_2Co^{II}]^{2+} + NH_3^+CH_2CH{=}NH_2^+ \qquad (11)$$

is accompanied by a decrease in conductivity because of the consumption of one $H^+$. This hydrolysis proceeds faster than the hydrolysis of en from a reduced $[Co(en)_3]^{2+}$ complex[2] because formation of a chelate ring is less likely with the imine ligand than with ethylenediamine. Organic imines are known to be unstable with respect to hydrolysis.[24] The released monoimine ligands will finally be hydrolyzed to ammonia and a 2-amino aldehyde by reaction 12. This reaction changes the conductivity only very little.

$$NH_3^+CH_2CH{=}NH_2^+ + H_2O \rightarrow NH_3^+CH_2CHO + NH_4^+ \qquad (12)$$

**(c) $[CoCl_2(en)_2]^+$.** Figure 3 shows oscillograms obtained in the $N_2O$-saturated *trans*-$[CoCl_2(en)_2]^+$ solution, after pulse irradiation. The increase of the conductivity in Figure 3a is due to the dissociation of two $Cl^-$ ions. A similar (but bigger) increase of the conductivity was described in the previous paper

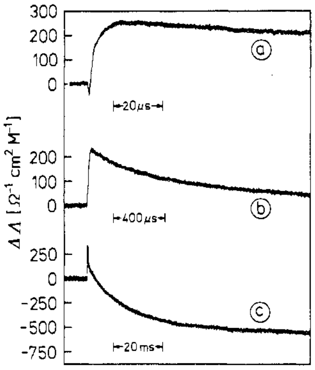


**Figure 3.** Oscilloscope traces of conductivity vs. time for the dissociation after pulse irradiation of $N_2O$-saturated $[CoCl_2(en)_2]^+$ solution at pH 3.7.

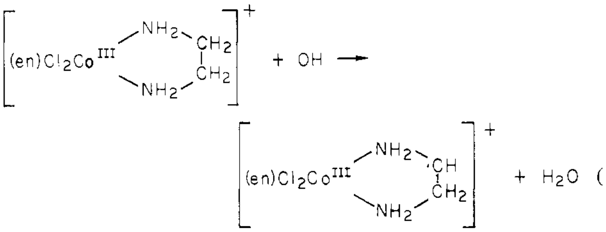
on the pulse radiolysis of argon-saturated $[CoCl_2(en)_2]^+$–*t*-BuOH system.[2] In this case reactions 13 and 14 occur, which

$$[CoCl_2(en)_2]^+ + e_{aq}^- \rightarrow [CoCl_2(en)_2] \qquad (13)$$

$$[CoCl_2(en)_2] \rightarrow [Co(en)_2]^{2+} + 2Cl^- \qquad (14)$$

cause an increase of conductivity ($\Delta\Lambda_{obsd} = 610\ \Omega^{-1}\ M^{-1}\ cm^2$) due to the protons formed together with the hydrated electrons and the ions formed in eq 14.

The rate constant obtained from the curve in Figure 3a agreed with that obtained by the competitive method as shown in Table I. This suggests that the reaction of $[CoCl_2(en)_2]^+$ with the OH radical is the rate-determining step for the dissociation of $Cl^-$ ions from the central metal ion. The first decrease of conductivity in Figure 3b will be due to the dissociation of degraded en. The conductivity change corresponded to the uptake of one proton. Thus a similar mechanism to the case of $[Co(en)_3]^{3+}$ is suggested (eq 15 and 16).



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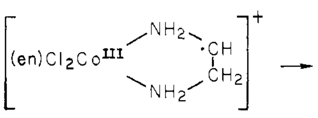


$$[(en)Co^{II}NH_2CH_2CH{=}NH_2]^{3+} + 2Cl^- \qquad (16)$$

Figure 4 shows the relationship between the dissociation rate constants of the degraded ligand and pH, together with that of an undegraded ligand. The results show that the dissociation rate of the degraded ligand is faster than that of the corresponding undegraded ligand. The dissociation reaction is expressed by reaction 17. The hydrolysis rate is nearly the same as for the oxidized $[Co(en)_3]^{3+}$ (Figure 2a).

$$[(en)Co^{II}NH_2CH_2CH{=}NH_2]^{3+} + H^+ \rightarrow [Co^{II}(en)]^{2+} + NH_3^+CH_2CH{=}NH_2^+ \qquad (17)$$

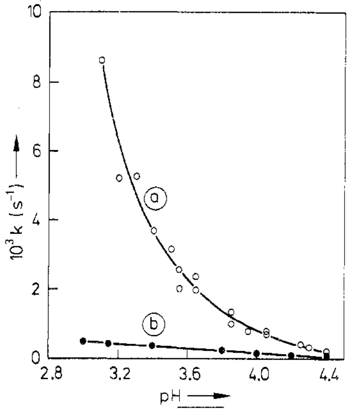


**Figure 4.** Plot of rate constants vs. pH for the dissociation of the first en for $[CoCl_2(en)_2]^+$: (a) $N_2O$ saturated, (b) *tert*-butyl alcohol added (from ref 2, no $N_2O$).

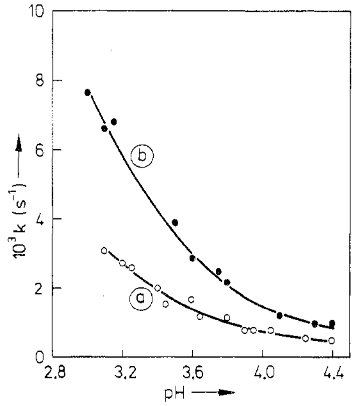
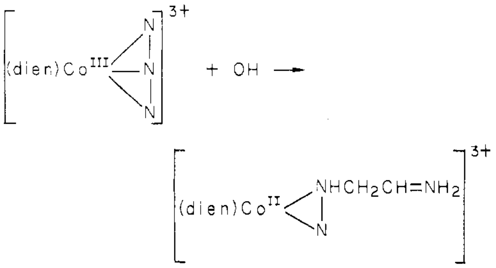


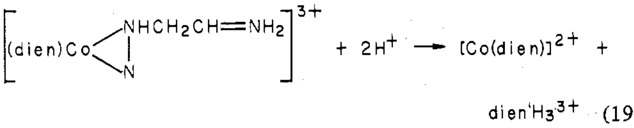
**Figure 5.** Plot of rate constants vs. pH for the dissociation of the first dien for $[Co(dien)_2]^{3+}$: (a) $N_2O$ saturated, (b) *tert*-butyl alcohol added (from ref 2, no $N_2O$).

**(d) Other Polyamine Complexes.** No conductivity change was observed immediately after the pulse irradiation of a $[Co(dien)_2]^{3+}$ solution saturated with $N_2O$. A mechanism analogous to that of $[Co(en)_3]^{3+}$ which does not involve an initial conductivity change is postulated in eq 18, where N-N-N denotes $NH_2CH_2CH_2NHCH_2CH_2NH_2$.



(18)

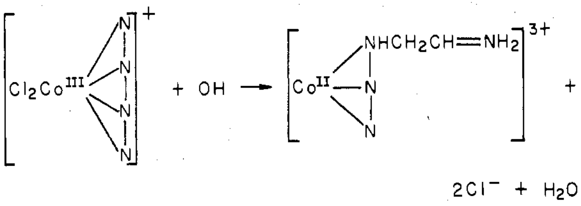
Subsequently two steps were observed in the dissociation of the oxidized complex. The magnitude of conductivity change for each step depends on pH. It is highest at low pH and becomes smaller toward pH 7. We have reported a similar pH dependence in the *tert*-butyl alcohol system[2] which was attributed to the small $pK_1$ of dien ($pK_1 = 4.34$, $pK_2 = 9.13$, $pK_3 = 9.98$[26]). The magnitude of the observed conductivity change induced by the dissociation of the degraded dien was smaller by the conductivity of one proton than that of undegraded dien. This suggests that the intermediate is already protonated. The dissociation reaction was first order and the rate constants for the first step are shown in Figure 5 as a function of pH. The dissociation rate of degraded dien is slower than that of undegraded dien. The reaction for the first step at low pH can be expressed by reaction 19, where dien′ denotes the degraded dien $NH_2CH_2CH_2NHCH_2CH{=}NH$. The C=N double bond is formulated at the terminal nitrogen because $NH_3$ was detected in the γ radiolysis of $[Co(dien)_2]^{3+}$



(19)

solutions ($G$ = 3.0) and a secondary imine would give no $NH_3$.[23]

In the reaction of $[CoCl_2(trien)]^+$ with OH radical, an increase of conductivity ($\Delta\Lambda = 330\ \Omega^{-1}\ M^{-1}\ cm^2$) was found after pulse irradiation. The reaction mechanism is expected to be similar to that of $[CoCl_2(en)_2]^+$ and is given in eq 20,



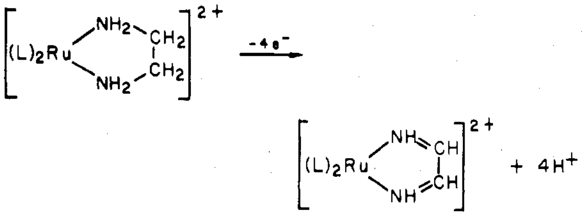
(20)

where N–N–N–N denotes $NH_2CH_2CH_2NHCH_2CH_2NH$-$CH_2CH_2NH_2$. Two steps were observed in the dissociation of the degraded trien as well as in that of undegraded trien in the *tert*-butyl alcohol system which we have reported.[2] The magnitude of the conductivity change for the first step was smaller than that in the $[CoCl_2(trien)]^+$–$t$-BuOH system as in the $[Co(dien)_2]^{3+}$ case. This is attributed to the protonated form of the intermediate from reaction 20. The dissociation reaction was first order and the rate constants for the first step are given as a function of pH in Figure 6. Also, in this case, the dissociation rate of degraded trien is a little slower than that of undegraded trien. The reaction for the first step will be expressed by (21), where trien′ denotes

$$[Co(trien'H)]^{3+} + 2H^+ \rightarrow [Co(trien'H_3)]^{5+} \qquad (21)$$

$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH{=}NH$. While the dissociation rate of degraded en was faster than the rate of undegraded en, the behavior is different in the case of dien and trien as ligands. There the dissociation of degraded ligands is slower than that of undegraded ligands. In contrast to degraded en in the latter cases chelate formation is still possible, because two or three amino groups are still available. Therefore the effect that the dissociation rate of amino ligands decreases with decreasing number of coordinated amines[1,2] becomes important. In the case of degraded dien or trien there is one less amine bound to the cobalt, and therefore a slower rate can be expected.

**(e) Comparison of Different Possible Mechanisms.** The oxidative dehydrogenation of coordinated amines to imines, catalyzed by metal ions such as $Ni^{2+}$, $Cu^{2+}$, $Fe^{2+}$, and $Ru^{2+}$, is assumed to proceed primarily by an oxidation of the central atom to the next higher oxidation state, followed by an oxidation of the ligands by two steps and an equivalent reduction of the central atoms.[4-12] For example, Ru(II)–en complexes have been reported to be oxidized to the diimine complexes chemically or electrochemically[8-10] as shown in eq 22, where



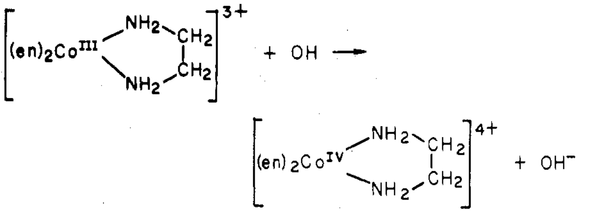
(22)

L is en or bipyridine. Complexes containing 1,2-diamino-2-methylpropane undergo net two-electron oxidation, in which the single $CH_2NH_2$ linkage undergoes oxidative dehydrogenation to the imine.[10] The oxidative dehydrogenation reactions have been reported to be initiated by oxidation of Ru(II) to Ru(III). In pulse irradiation of Cu(II)– and Ni(II)–en complexes, M(III) intermediates[11-13] have been reported to be produced by reactions 23 and 24. A similar reaction

$$[Cu(en)_2]^{2+} + OH \rightarrow [Cu(en)_2]^{3+} + OH^- \qquad (23)$$

$$[Ni(en)_n]^{2+} + OH \rightarrow [Ni(en)_n]^{3+} + OH^- \qquad (24)$$

involving oxidation of the metal ion followed by oxidation of the ligand and reduction of the metal ion could be proposed for the case of OH attack to $[Co(en)_3]^{3+}$ since OH radical is a very strong oxidant



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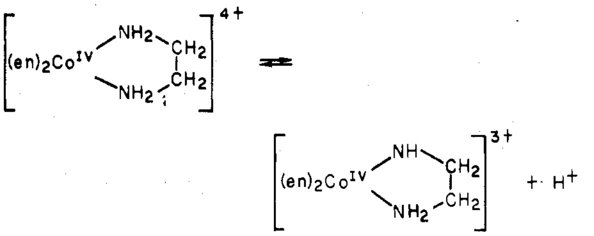

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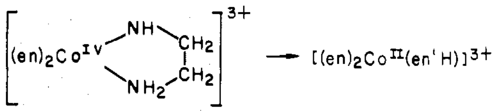

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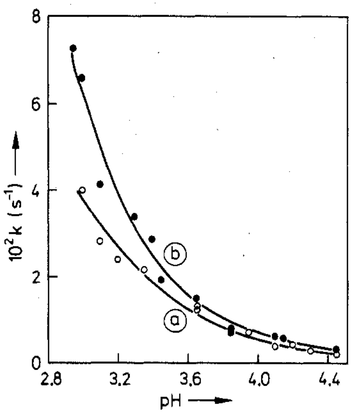

**Figure 6.** Plot of rate constants vs. pH for the first step of dissociation of trien for $[CoCl_2(trien)]^+$: (a) $N_2O$ saturated, (b) *tert*-butyl alcohol added (from ref 2, no $N_2O$).

If $[Co(en)_3]^{4+}$ is relatively stable, the conductivity must be decreased by the very rapid consumption of proton by $OH^-$ from the reaction (25) immediately after pulse irradiation. But such a conductivity change could not be observed in the examined pH region. Thus deprotonation such as reaction 26 will be essential for interpreting the results of the conductivity measurements which must be followed by intraelectron transfer for the rapid detachment of degraded ligand (reaction 27).

Reaction 26 is essential to explain the result of conductance measurement, and the p$K$ of this equilibrium must be less than 2 for complete deprotonation in the examined pH region. But this value seems to be too small. In the $\gamma$ radiolysis of an acidic solution of $[Co(en)_3]^{3+}$, $G(H_2)$ was found to be 3.2,[23] and also in the reaction of tris(glycinato)cobaltate(III) with H atoms, Schagisultanova et al.[26] have detected molecular hydrogen as product. These facts indicate that H atoms abstract hydrogen from the ligand of Co(III) complexes without reducing Co(III) to Co(II) directly. The OH radical is a very strong oxidant and also a very good hydrogen abstractor for a number of saturated organic substances. These facts suggest that hydrogen abstraction is more plausible for the reaction of $[Co(en)_3]^{3+}$ with OH radical, different from that for Cu(II) or Ni(II) complexes.

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**Registry No.** $[Co(en)_3]^{3+}$, 14878-41-2; $[Co(dien)_2]^{3+}$, 18703-28-1; $[CoCl_2(en)_2]^+$, 15275-04-4; $[CoCl_2(trien)]^+$, 46135-19-7; OH radical, 3352-57-6.

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# Fitting of Nickel(II) Ion into the Two 14-Membered Tetraaza Macrocycles. Blue-to-Yellow Conversion and the Oxidation and Reduction Behavior

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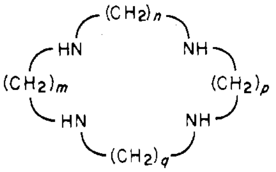
The novel saturated tetraaza macrocycle *isocyclam* (**2**) has been synthesized and the behavior of its nickel(II) complexes, which contain a 5,5,6,6 sequence of chelate rings, is compared with that of corresponding complexes of *cyclam* (**1**) (sequence: 5,6,5,6). These complexes exist in solution as a mixture of blue, octahedral, high-spin and yellow, planar, low-spin species; the thermodynamic parameters for the blue-to-yellow conversion depend upon the cyclic nature of the ligand. In analogy with $Ni(cyclam)^{2+}$, $Ni(isocyclam)^{2+}$ undergoes one-electron oxidation and reduction processes at a platinum electrode in acetonitrile. The easier reduction and more difficult oxidation of both blue and yellow 5,5,6,6 complexes with respect to the 5,6,5,6 analogues have been related to the differences in the in-plane Ni–N interaction parameters, as inferred from electronic spectra. General redox behavior of Ni(II) complexes with tetraaza macrocycles has been reconsidered and a linear correlation between oxidation and reduction potentials is presented.

## Introduction

The growing interest in synthetic tetraaza macrocycles and their metal complexes depends (i) on the fact that they may mimic naturally occurring macrocyclic molecules in their structural and functional features and (ii) on their rich chemical behavior. Since the pioneering work of Curtis[1] and Busch[2] on the template syntheses of both saturated and unsaturated macrocycles, preparative improvements have now made available a complete series of saturated and unsubstituted 12- to 16-membered cyclic tetramine ligands.[3-5]



$m = n = p = q = 2$ [12]ane$N_4$
$m = n = p = 2; q = 3$ [13]ane$N_4$
$m = p = 2; n = q = 3$ [14]ane$N_4$ or *cyclam*
$m = 2; n = p = q = 3$ [15]ane$N_4$
$m = n = p = q = 3$ [16]ane$N_4$

These ligands have a strong tendency to encircle in a coplanar fashion 3d metal ions, forming a unique family of complexes in which the strength of the in-plane metal–nitrogen interactions is modulated according to the size of the ligand aperture. It has been predicted, on the basis of conformational arguments,[6] that the size of the 14-membered macrocycle, [14]-ane$N_4$, previously named *cyclam*,[7] is almost exactly that required by the divalent first-row transition-metal ions, larger and smaller ligands of the series being too large and too small. This prediction has been confirmed by both spectrochemical and thermochemical studies: in fact (i) cyclam establishes the highest in-plane $Dq$ with copper(II)[8] and high-spin nickel(II),[5] and (ii) it gives the most exothermic metal–ligand enthalpies[9,10] (this latter property being coresponsible for the exceptionally high solution stablity, the so-called thermodynamic *macrocyclic effect*).[11]

The favorable size requirements and sequence of chelate rings of cyclam are further demonstrated by the fact that template syntheses work well mainly when a cyclam-like structure is involved.[12-14]

It must be pointed out that, in the series of cyclic tetraaza ligands under consideration, the 14-membered example is

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