also admit two possible explanations. Taube[12] has suggested that the similarity of the activation energies for the reactions $H_3O^+ + Cr(H_2O)_5OAc^{2+} \rightarrow Cr(H_2O)_6^{3+} + HOAc$ (19 kcal mol^{-1}) and $H_3O^+ + CH_3OAc \rightarrow CH_3OH + HOAc$ (16.4 kcal mol^{-1}), which must involve C–O fission, indicates that the acetatochromium(III) complex aquates with carbon–oxygen fission. It is of interest to note that the activation energy for the *cis*-$[Co(en)_2(OAc)_2]^+$ complex falls closely into this category. However, there are many examples in cobalt ammine chemistry where the entropy of activation for the aquation of a *cis*-diacidotetraamine is considerably less positive (or more negative) than that of its trans isomer and in most of these cases the activation energy is significantly lower as well.[15–19] In all of these cases (Table VI) the trans isomer aquates with stereochemical change but there is no possibility of fission other than at the Co–X bond. Apart from its unusually low activation energy (not unknown in cobalt ammine chemistry), the *cis*-$[Co(en)_2(OAc)HOAc]^{2+}$ complex fits this behavior reasonably well. At this stage, therefore, we consider the mechanism of the acid-catalyzed aquation of *cis*-$[Co(en)_2(OAc)_2]^+$ to be still in some doubt, but, until the isotopic labeling or other convincing experiments cause us to believe the contrary, we can find no reason why the *cis*-diacetato complex should be mechanistically so different from its trans isomer and prefer to assign a dissociative mechanism with Co–O bond fission to them both.

TABLE VI

ACTIVATION PARAMETERS FOR AQUATION OF SOME CIS–TRANS ISOMERIC PAIRS IN WHICH THE TRANS ISOMER AQUATES WITH STERIC CHANGE

	$\Delta H^\ddagger$, kcal mol^{-1}		$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}		
Complex	Cis	Trans	Cis	Trans	Ref
$[Co(en)_2(OAc)(HOAc)]^+$	15.4	23.0	−13	+1	This work
$[Co(en)_2Cl_2]^+$	21.5	26.2	−5	+14	14, 15
$[Co(en)_2NCSCl]^+$	20.1	30.2	−14	+9	16, 17
$[Co(en)_2NCSBr]^+$	23.1	30.1	−5	+11	16, 17
$[Co(trien)Cl_2]^+$	21.0[a]	25.5	−6[a]	+16	18
	20.3[b]		−3[b]		

[a] α-Cis. [b] β-Cis.

In his studies of the isomerization and acetate exchange of *cis*- and *trans*-$[Co(en)_2(CH_3COO)_2]^+$ in glacial acetic acid, Chester[8] has suggested that the *trans*-diacetato complex isomerizes intramolecularly to the cis which then undergoes a rapid exchange reaction with the solvent acetic acid. In view of the great difference in reactivity of the *cis*- and *trans*-$[Co(en)_2(CH_3COO)_2]^+$ isomers, such a mechanism cannot be ruled out in aqueous solution on the basis of the kinetic data alone. However, it has been shown quite clearly that the aquation of the trans complex yields 75% *cis*-aquoacetato product. If aquation went by way of the labile cis isomer, this should have yielded 100% cis product. In any case, there are no precedents for an acid-catalyzed intramolecular isomerization in cobalt(III) complexes of this type, and since it does not seem reasonable that change in solvent from dilute perchloric acid to pure acetic acid should promote an intramolecular isomerization, we would view Chester's mechanism with some caution.

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Kinetics and Mechanism of the Reductions of *cis*- and *trans*-Diformatobis(ethylenediamine)cobalt(III) by Vanadium(II)[1]

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The reductions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ by V(II) obey the rate law $-d[Co(III)]/dt = k_2[Co(III)][V(II)]$ when $[H^+]$ is constant. The second-order rate coefficients k_2 have been measured as a function of $[H^+]$ in the range 0.11–0.91 *M*. For the trans complex k_2 is independent of $[H^+]$ and has the value $k_{trans} = 13.0 \pm 0.2\ M^{-1}\ sec^{-1}$ at 25°. For the cis complex k_2 decreases with increasing $[H^+]$ according to $k_2 = k_{cis}/(1 + Q[H^+])$. At 25° $k_{cis} = 14.8 \pm 0.2\ M^{-1}\ sec^{-1}$ and $Q = 0.17 \pm 0.03\ M^{-1}$. The activation parameters associated with k_{cis} and k_{trans} are $\Delta H^\ddagger(cis) = 10.9 \pm 0.6$ kcal mol^{-1}, $\Delta H^\ddagger(trans) = 11.0 \pm 0.2$ kcal mol^{-1}, $\Delta S^\ddagger(cis) = -16.7 \pm 1.9$ eu, and $\Delta S^\ddagger(trans) = -20.2 \pm 0.6$ eu. An inner-sphere, substitution-controlled mechanism is suggested to account for the results. Comparisons of the Cr(II) and V(II) reductions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ are made, and an indirect criterion for mechanistic assignments is tentatively proposed.

Introduction

The effect of nonbridging ligands on the rates of oxidation–reduction reactions of transition metal complexes has been the subject of several recent papers.[2] Most of the previous work involving inner-sphere mechanisms has been carried out with systems for which the rate of the electron-transfer step is slower than the rate of formation of the precursor binuclear complex.[3] In the present work, we report the kinetics of the reductions of *cis*- and *trans*-diformatobis(ethylenediamine)cobalt(III) by vanadium(II). The choice of these particular reactants was dictated by two considera-

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(1) This work was supported by Grant GP-9669 from the National Science Foundation.

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TABLE I

KINETICS OF THE REACTION OF *cis*-$Co(en)_2(HCO_2)_2^+$ WITH VANADIUM(II)[a]

$10^2[V^{2+}]$, *M*	$[H^+]$, *M*	$10k_{obsd}$,[b] sec^{-1} 15°	25°	35°	k_2,[c] M^{-1} sec^{-1} 15°	25°	35°
1.69	0.11	1.36	2.21, 2.43, 2.46 2.63, 1.91[d]	4.78	8.1	13.0, 14.3, 14.5 15.8, 11.3[d]	28.1
1.69	0.50	1.10	2.41	4.30, 4.55	6.4	13.9	24.6, 26.3
1.88	0.50	1.51, 1.36[e]			8.07, 7.2		
0.85	0.50			2.16, 2.17			23.8, 24.0
3.38	0.50			9.60			27.9
1.88	0.91	1.23			6.4		
1.69	0.91		2.24, 2.26	4.05, 4.11		12.7, 12.9	22.6, 22.9

[a] Measurements at 270 nm, $[ClO_4] = 2.0$ *M* adjusted with $LiClO_4$, $[Co(III)] = (2.5–5.0) \times 10^{-4}$ *M*. [b] Pseudo-first-order rate coefficients defined by $-d[Co(III)]/dt = k_{obsd}[Co(III)]$. Each entry is the average of three to five replicate measurements with the same pair of solutions. [c] Second-order rate coefficient defined by eq 1. [d] $[ClO_4^-] = 1.0$ *M*. [e] Measurement at 290 nm.

tions. First, the rates of inner-sphere reactions of vanadium(II) have been shown to depend primarily on the substitution of water in the coordination sphere of vanadium(II) by the bridging ligand, the subsequent electron-transfer step being rapid.[3] Second, the reactions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ with chromium(II) have been studied previously,[4] and they display rather dramatically the difference between cis and trans positions in electron-transfer-controlled, inner-sphere redox reactions of complexes containing the conjugate base of a weak acid as the nonbridging ligand.

Experimental Section

Materials.—*cis*- and *trans*-$[Co(en)_2(HCO_2)_2](ClO_4)$ were prepared and recrystallized following the procedure of Linhard and Stirn.[5] The cis complex exhibited maxima at 500 and 362 nm with molar absorptivities 127 and 84.7, respectively. The trans complex displayed maxima at 539, 452, and 356 nm with molar absorptivities 51.3, 29.9, and 66.4, respectively. The values obtained in the present work are in excellent agreement with those reported previously.[4] *cis*-Aquoformatobis(ethylenediamine)cobalt(III) perchlorate was prepared *in situ* by the stereospecific acid-catalyzed aquation of the *cis*-diformato complex (the half-life at 25° and $[HClO_4] = 1.0$ *M* is *ca.* 80 sec).[6]

Vandium(II) perchlorate solutions were prepared by reduction of solutions of vanadium(V) oxide in perchloric acid with amalgamated zinc under continuous purging with argon. The vanadium(V) content of the solutions prior to reduction was determined by titration with freshly prepared iron(II) solutions.[7] Since the reduction of vanadium(V) by amalgamated zinc is quantitative,[8] the vanadium(II) concentration was taken to be equal to that of vanadium(V). The free perchloric acid concentration of the vanadium(V) solutions was determined indirectly. An aliquot of the vanadium(V)–perchloric acid solution was mixed with a known excess of iron(II) sulfate, and then the product mixture was added to a column of Dowex 50W-X2 resin in the hydrogen ion form. The iron(III) and vanadium(IV) were taken up by the resin, and the acid liberated plus the free acid were titrated. The free perchloric acid concentration was calculated by subtracting the acid equivalent to the iron and vanadium from the total acid.

The preparation of lithium perchlorate solutions and the purifications of the argon and of the water have been described previously.[4,9]

Kinetic Measurements.—The kinetic measurements were carried out in a stopped-flow apparatus.[10] The oscilloscope was connected to an IBM 1800 computer. Thirty voltage measurements were acquired during the first 4 half-lives, followed by six voltage measurements at 1-half-life intervals. The voltages were converted to oscilloscope readings by means of a calibration curve, and the readings were processed using a least-squares program as described previously.[4] First-order kinetics were assumed in the computations since the vanadium(II) was in large excess with respect to the cobalt(III). In order to minimize any aquation of the cobalt(III) complex prior to reaction, all the desired acid was contained in the vanadium(II) solution. The cobalt(III) solution contained lithium perchlorate to adjust the ionic strength to the desired value. Three to five replicate measurements were carried out for each pair of solutions.

Results

The results of the kinetic measurements for the *trans*- and *cis*-$Co(en)_2(HCO_2)_2^+$–V^{2+} reactions are summarized in Tables I and II. Excellent pseudo-first-order kinetics were obeyed over 4 half-lives. The observed pseudo-first-order rate constants are listed in columns 3–5 of Tables I and II. In order to calculate the rate coefficients defined by the rate equation

$$\frac{-d[Co(III)]}{dt} = k_2[Co(III)][V^{2+}] \qquad (1)$$

where k_2 is the second-order rate coefficient for reduction of Co(III) by V(II), the observed pseudo-first-order rate constants had to be corrected for the acid-catalyzed aquations of the cobalt(III) complexes. In the case of the trans isomer, the correction amounts to less than 0.1%,[11] and therefore it was neglected. However, in the case of cis complex, the contribution of the acid-catalyzed aquation to the total disappearance of the complex is significant, varying between ~0.4% at $[H^+] = 0.11$ *M* and ~4% at $[H^+] = 0.91$ *M*.[12] The product of the aquation is *cis*-$Co(en)_2(OH_2)(HCO_2)^{2+}$ which also reacts with vanadium(II). The second-order rate constant for the *cis*-$Co(en)_2(OH_2)(HCO_2)^{2+}$–$V^{2+}$ reaction was measured at 25°, $[H^+] = 1.0$ *M*, and $[ClO_4^-] = 2.0$ *M* and was found to be 8.4 ± 0.5 M^{-1} sec^{-1}. It can be shown that under the most unfavorable circumstances (lowest $[V^{2+}]$ and highest $[H^+]$), the concentration of *cis*-$Co(en)_2(OH_2)(HCO_2)^{2+}$ builds up only to a maximum of 1.8% of the initial *cis*-$Co(en)_2(HCO_2)_2^+$ concentration. Therefore, the observed pseudo-first-order rate constant k_{obsd} for disappearance of *cis*-$Co(en)_2(HCO_2)_2^+$ was taken to be $k_H + k_V$, where k_H and k_V are the pseudo-first-order rate constants for acid-catalyzed aquation and vanadium(II) reduction, respectively. The second-order rate coefficients, calculated from the expression $k_2 = (k_{obsd} - k_H)/[V^{2+}]$, are listed in the last three columns of Tables I and II. It is

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(4) J. R. Ward and A. Haim, *J. Amer. Chem. Soc.*, **92**, 475 (1970).

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(9) B. Grossman and A. Haim, *J. Amer. Chem. Soc.*, **93**, 6490 (1971).

(10) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(11) The rate of acid-catalyzed aquation of *trans*-$Co(en)_2(HCO_2)_2^+$ is given by the expression $k[Co(III)][H^+]$ where $k \approx 10^{-4}$ M^{-1} sec^{-1} at 40° and ionic strength 1.0 *M*.

(12) The rate of the acid-catalyzed aquation of *cis*-$Co(en)_2(HCO_2)_2^+$ is given by the expression[6] $k_{aq}[H^+][Co(III)]/(1 + Q[H^+])$, with $k_{aq} = 3.24 \times 10^{-2}$ sec^{-1} and $Q = 0.36$ at 25° and 1.0 *M* ionic strength.

TABLE II

KINETICS OF THE REACTION OF *trans*-$Co(en)_2(HCO_2)_2^+$ WITH VANADIUM(II)[a]

$10^2[V^{2+}]$, M	$[H^+]$, M	k_2,[b] M^{-1} sec^{-1} 15°	25°	35°
1.69	0.11		13.0, 13.3, 10.1[c]	25.1
1.88	0.11	6.2		
1.69	0.50		12.8, 13.0[d]	24.4
1.88	0.50	6.6, 6.6, 6.7		
0.85	0.50			25.6
3.38	0.50			25.1
1.69	0.91		12.6	24.6
1.88	0.91	6.6		

[a] Measurements at 270 nm, $[ClO_4^-] = 2.0\ M$ adjusted with $LiClO_4$, $[Co(III)] = (2.5–5.0) \times 10^{-4}\ M$. [b] Second-order rate coefficient defined by eq 1. [c] $[ClO_4^-] = 1.0\ M$. [d] Measurement at 534 nm with $[Co(III)] = 1.89 \times 10^{-3}\ M$ and $[V^{2+}] = 1.64 \times 10^{-2}\ M$.

seen that for the trans complex, k_2 is independent of $[V^{2+}]$ and $[H^+]$, and therefore the mixed second-order rate law given by eq 1 adequately describes the kinetics of the *trans*-$Co(en)_2(HCO_2)_2^+$–V^{2+} reaction. From the temperature dependence of k_2, the following activation parameters are calculated: $\Delta H^\ddagger = 11.0 \pm 0.2$ kcal mol^{-1} and $\Delta S^\ddagger = -20.2 \pm 0.6$ eu. For the cis complex, k_2 is independent of $[V^{2+}]$, and again eq 1 describes adequately the kinetics of the *cis*-$Co(en)_2(HCO_2)_2^+$–V^{2+} reaction, except for any possible acid dependence. However, in contrast with the findings for the trans complex, the values of k_2 for the cis complex decrease with increasing acidity. The variation in $[H^+]$ is not sufficiently extensive to define the $[H^+]$ dependence of k_2. However, the observed variations are entirely consistent with the form previously found[4] in the analogous *cis*-$Co(en)_2(HCO_2)_2^+$–Cr^{2+} reaction. Guided by the previous functional form, the values of k_2 were fitted to the expression $k_{cis}(1 + Q_{cis}[H^+])$. The values of k_{cis} (M^{-1} sec^{-1}) and Q_{cis}, computed using a nonlinear least-squares program, were found to be 8.4 ± 0.1 and 0.33 ± 0.01, 14.8 ± 0.2 and 0.17 ± 0.03, and 29.0 ± 0.2 and 0.30 ± 0.01 at 15, 25, and 35°, respectively. From the temperature dependence of k_{cis}, the following activation parameters are calculated: $\Delta H^\ddagger = 10.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = -16.7 \pm 1.9$ eu.

Discussion

The results of the kinetic measurements of the vanadium(II) reductions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ conform to the mechanistic scheme

$$\begin{array}{c} cis\text{- or } trans\text{-}Co(en)_2(HCO_2)_2^+ + H^+ \overset{Q}{\rightleftharpoons} \\ \qquad\qquad cis\text{- or } trans\text{-}Co(en)_2(HCO_2)_2H^{2+} \\ V^{2+}\Big\downarrow k_{cis} \text{ or } k_{trans} \\ \text{products} \end{array} \qquad (2)$$

Equation 2 represents a rapid acid–base equilibrium governed by an equilibrium quotient Q, and k_{cis} or k_{trans} is the second-order rate constant for the V^{2+} reduction of the nonprotonated diformato complex. On the basis of this mechanism, the measured second-order rate coefficient k_2 is given by

$$k_2 = \frac{k_{cis}}{1 + Q_{cis}[H^+]} \text{ or } \frac{k_{trans}}{1 + Q_{trans}[H^+]} \qquad (3)$$

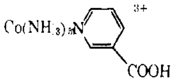
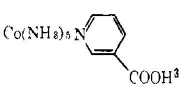
The cis complex follows rate law 3, as stated; for the trans complex, protonation in the range studied is negligible, and the denominator in eq 3 approaches unity.

The extent of protonation for the cis and trans complexes measured in the present work is in excellent agreement with previous measurements[4,6,12] based on the Cr(II) reduction of the diformato complexes or their acid-catalyzed aquations. The agreement for three systems that exhibit radically different chemistries[13] lends strong support to the proposed reaction sequence.

The rate constants and corresponding activation parameters for the reductions of a series of carboxylatocobalt(III)–ammine complexes are presented in Table III. It will be seen that the second-order rate constants (25°) and activation energies fall in the narrow ranges 1–45 M^{-1} sec^{-1} and 12.4 ± 1.5 kcal/mol, respectively. It has been suggested previously that these values may be taken as diagnostic of an inner-sphere mechanism for vanadium(II) reactions,[14–16] and therefore we infer that the reactions of *cis*- and *trans*-$Co(en)_2(HCO_2)_2^+$ with V^{2+} proceed *via* an inner-sphere mechanism. Of the three stages usually considered in an inner-sphere mechanism[14] (L is a uninegative bridging ligand, M(III) and N(II) are the oxidant and reductant, respectively)—formation of precursor complex

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REDUCTION OF CARBOXYLATOCOBALT(III) COMPLEXES BY VANADIUM(II)

Complex	k,[a] M^{-1} sec^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	ΔS, eu	Ref
$Co(NH_3)_5(HCO_2)^{2+}$	3.6	13.9	−13	*b*
$Co(NH_3)_5(CH_3CO_2)^{2+}$	1.2	11.6	−19	*b*
cis-$Co(en)_2(HCO_2)_2^+$	7.4[c,d]	10.9	−17	*e*
cis-$Co(en)_2(H_2O)(HCO_2)^{2+}$	8.4[c]	...	...	*e*
trans-$Co(en)_2(HCO_2)_2^+$	6.5[c,d]	11.0	−20	*e*
$Co(NH_3)_5(C_2O_4H)^{2+}$	12.5	12.2	−13	*f*
$Co(NH_3)_4C_2O_4^+$	45	12.3	−10	*g*
	7.1	...	...	*h*
	5.3	...	...	*h*

[a] At 25° and 1.0 M ionic strength. [b] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). [c] Ionic strength 2.0 M. [d] Observed rate constant divided by 2 to correct for statistical factor. [e] This work. [f] H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968). [g] C. Hwang and A. Haim, *ibid.*, **9**, 500 (1970). [h] C. Norris and F. Nordmeyer, *ibid.*, **10**, 1235 (1971).

$$ML^{2+} + N^{2+} \rightleftharpoons MLN^{4+} \qquad (4)$$

electron transfer

$$MLN^{4+} \rightleftharpoons MLM^{4+} \qquad (5)$$

and dissociation of successor complex

$$MLN^{4+} \rightleftharpoons M^{2+} + NL^{2+} \qquad (6)$$

the substitution step 4 is taken to be rate limiting in

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(13) The Cr^{2+} reduction and the acid-catalyzed aquation of the trans complex are accelerated by acid, whereas the V^{2+} reduction is $[H^+]$ independent. The Cr^{2+} and V^{2+} reductions of the cis complex are inhibited by acid, whereas the acid-catalyzed aquation increases in rate with increasing $[H^+]$.

(14) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(15) C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970).

(16) If the rate constants are divided by the number of remote oxygen atoms on the carboxylate ligands, then the even narrower range 1–22 M^{-1} sec^{-1} is obtained.

vanadium(II) reductions. The narrow range of second-order rate constants for the various carboxylate complexes indicates that the rate of substitution on vanadium(II) is governed principally by the loss of water and that there is little or no assistance by the incoming carboxylate.

Two of the most significant aspects of the present investigation pertain to the contrast between the rate laws for V^{2+} and Cr^{2+} reduction of *trans*-$Co(en)_2(HCO_2)_2^+$ and to the relative reactivities of cis and trans isomers toward reduction by V^{2+} or Cr^{2+}. The reaction of *trans*-$Co(en)_2(HCO_2)_2^+$ with V^{2+} is independent of $[H^+]$, whereas the corresponding reaction with Cr^{2+} features an important term first order in H^+.[4] The reactions of the cis or trans isomers with V^{2+} are virtually identical; whereas a strong discrimination between the two isomers is observed for the Cr^{2+} reductions.[4] On the basis of eq 4–6 the contrasting behavior between reductions by V^{2+} and Cr^{2+} is readily understood. For the Cr^{2+} reactions, the electron-transfer step (eq 5) is rate determining. This step requires changes in the inner coordination shells and electronic energy levels of the two metal centers. Since protonation of the trans ligand on the oxidant appears to have the effect of facilitating such changes and lowering the energy of the acceptor orbital,[4,17] it is readily seen that the reactivity of the oxidant will increase on protonation. With V^{2+} as the reductant, the formation of the precursor binuclear complex appears to be rate determining (eq 4), and in this step no major reorganization is necessary in the coordination shell of the oxidant—only the ability of the bridging ligand to substitute into the coordination shell of V^{2+} is important—and consequently it is reasonable that no acceleration by H^+ obtains in this system. The difference in relative reactivities of the isomers toward V^{2+} or Cr^{2+} can also be understood on the basis of the shift in rate-determining step in going from one reductant to the other. In Cr^{2+} reductions, the nature of the ligand trans to the bridging group is important, since it changes the energy of the acceptor orbital and consequently determines the reactivity,[18] whereas for V^{2+} reductions the dissociative character of the rate-determining substitution makes these reactions rather insensitive to the nonbridging ligands in the oxidant.

Of three possible mechanistic classes, namely, inner-sphere rate-determining substitution, inner-sphere rate-determining electron transfer, and outer sphere, the presence or absence of an H^+ path for the trans isomers appears to provide a clear distinction between the two types of inner-sphere mechanisms and may provide a useful, but indirect, criterion for mechanistic assignment. However, until the patterns of hydrogen ion dependences for cis and trans isomers in outer-sphere reactions are established,[19] any mechanistic conclusions based on the presence or absence of an H^+ path must be considered tentative.

[17] A. Haim, *J. Amer. Chem. Soc.*, **86**, 2352 (1964).

[18] P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

[19] It has been reported that the reductions of both *cis* and *trans*-$Co(NH_3)_4(CH_3CO_2)_2^+$ by the outer-sphere reductant $Ru(NH_3)_6^{2+}$ feature a term first order in $[H^+]$: J. F. Endicott and H. Taube, *ibid.*, **86**, 1686 (1964). However, the authors expressed some doubt about the reliability of the H^+-dependent term for the cis complex, and additional work is necessary.

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An Extended Hückel Study of the Conformational Dependence of the Contact Shifts of Ethylenediamine Complexes of Nickel(II)

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Extended Hückel molecular orbital calculations have been used to calculate the ratio of the equatorial to axial contact shifts for puckered ethylenediamine chelate rings in Ni(II) complexes as a function of ring pucker. The results indicate that the ethylenediamine rings are less puckered in H_2O solution than they are in the solid state. Substitution of a methyl group on one of the amino nitrogens is found to produce a larger contact shift for the α-methylene group while little effect is noticed at the β-methylene group.

Introduction

Recently there has been considerable interest in the study of the conformations of chelating ligand rings by nmr.[1-4] In particular, for paramagnetic complexes, the nmr contact shift has been observed to be quite different for the axial and equatorial protons of puckered chelate rings,[5,6] even though the rings are in rapid equilibrium between the δ and λ conformations. By the use of careful temperature measurements Reilley and coworkers have been able to extract the equilibrium constants for the conformational $\delta \leftrightarrow \lambda$ interconversion, as well as the contact shifts for the "frozen" conforma-

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[3] J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

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[5] K. I. Zamaraev, Yu. N. Molin, and G. I. Skubnevskaya, *Zh. Strukt. Khim.*, **7**, 798 (1966); *J. Struct. Chem.*, **7**, 740 (1966).

[6] (a) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969). (b) We will assume the Λ configuration for the metal ion. Since both enantiomers give the same nmr spectrum in the absence of an optically active solvent, our results for a δ ring in a Λ complex also apply to a λ ring in a Δ complex.