that have been observed are those in Co(*trans*-diene)(ClO_4) between 1545 and 1590 cm^{-1}. These are also assigned to C=N but the reason for the shift is not clear. The frequencies are reproducible and the material was shown to be undecomposed Co(*trans*-diene)(ClO_4) by its electrochemistry.

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Reduction of Pentaamminecobalt(III) Complexes of Pyridinecarboxylic Acids by Remote Attack of Vanadium(II)

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The specific rates of reduction of N-coordinated (nicotinic acid)- and (isonicotinic acid)pentaamminecobalt(III) complexes by vanadium(II) have been studied as a function of hydrogen ion concentration at 25°. For both complexes the rates of reduction conform to the equation $-d(Co(III))/dt = [a + b/(c + (H^+))](Co(III))(V^{2+})$, where $a = 1.0\ M^{-1}\ sec^{-1}$, $b = 0.25\ sec^{-1}$, and $c = 0.035\ M$ for the nicotinic acid complex and $a = 1.4\ M^{-1}\ sec^{-1}$, $b = 0.97\ sec^{-1}$, and $c = 0.18\ M$ for the isonicotinic acid complex. It is proposed that the second term in the rate equation for these Co(III) complexes arises from attack of V^{2+} at the remote carboxylic acid function, with the formation of a binuclear intermediate which is in steady-state equilibrium with reactants and which, in a deprotonated form, undergoes electron transfer to form products.

Introduction

Recent studies of cobalt(III), chromium(III), and ruthenium(III) complexes of substituted pyridines have shown that their reductions by chromium(II) may proceed *via* remote attack.[1,2] These studies have yielded interesting conclusions concerning the effect of the symmetry of the acceptor orbital upon the mechanism of the electron transfer. In this article we report the reductions of similar complexes by vanadium(II) in which remote attack is an important pathway for reduction. Studies of reactions of this kind in which V^{2+} is the reductant provide a way to investigate the influence of the donor orbital on the electron-transfer mechanism.

Experimental Section

Pyridine-, nicotinamide-, and isonicotinamidepentaamminecobalt(III) perchlorate were prepared as described previously.[1]

Pentaamminecobalt(III) complexes of nicotinic acid and isonicotinic acid (structures I and II) were prepared from the corresponding amide complexes. About 5 mmol of the appropriate pentaamminecobalt(III) perchlorate was dissolved in a minimum of trimethyl phosphate and treated with small portions of nitrosyl perchlorate until gas evolution ceased. The acid complex was isolated from the reaction mixture as the iodide salt by diluting the trimethyl phosphate solution with a few volumes of water and adding sodium iodide. The light-sensitive iodide was converted to the perchlorate by treatment with silver perchlorate in aqueous solution. This salt was isolated by concentrating the solution by rotary evaporation and adding perchloric acid. The salt was purified by recrystallization from perchloric acid solutions. The complexes were also isolated in their deprotonated forms by crystallization from a solution adjusted to pH 6.

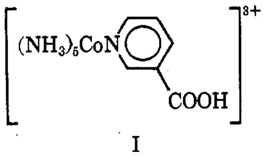
Anal. Calcd for $[(NH_3)_5CoNC_5H_4COOH](ClO_4)_3$: C, 12.74; H, 3.56; N, 14.86; Cl, 18.80; Co, 10.42. Found for (isonicotinic acid)pentaamminecobalt(III) perchlorate: C, 12.85; H, 3.74; N, 14.55; Cl, 18.8; Co, 10.3. Calcd for $[(NH_3)_5CoNC_5H_4COOH](ClO_4)_3 \cdot H_2O \cdot HClO_4$: C, 10.53; H, 3.39; N, 12.29; Cl, 20.73; Co, 8.62. Found for the (nicotinic acid)pentaamminecobalt(III) perchlorate: C, 10.65; H, 3.53; N, 12.38; Cl, 19.5; Co, 8.9.

Acid dissociation constants of complexes I and II were determined spectrophotometrically at 25°. Ultraviolet spectra of the acidic and basic forms of each complex were obtained in 1 M $HClO_4$ and in a solution of 0.01 M $NaHCO_3$ and 1 M $LiClO_4$ (pH 8). Seven different equilibrium mixtures of the acidic and basic forms were prepared in $HClO_4$ solutions and chloroacetic acid buffer solutions. Absorbance and pH measurements were made simultaneously on portions of the same equilibrium mixture. All solutions were made up from a single stock solution of cobalt(III) and were adjusted to 1 M ionic strength using $LiClO_4$. The hydrogen ion concentrations of the buffer solutions were obtained from pH readings using a glass electrode after the manner of Deutsch.[3] Readings obtained from solutions of known concentrations of $HClO_4$ were used to calibrate this method. K_a was evaluated from absorbance measurements, $A_{\lambda,i}$, of each equilibrium mixture according to the equation

$$K_a = (H^+)_i\left[\frac{A_{\lambda,acid} - A_{\lambda,i}}{A_{\lambda,i} - A_{\lambda,base}}\right]$$

$A_{\lambda,acid}$ and $A_{\lambda,base}$ refer to the absorbance of the complex at pH 0 and 8, respectively. For the complex of nicotinic acid, measurements at 272 and 256 nm gave $K_a = (2.7 \pm 0.4) \times 10^{-3}$ and $(2.7 \pm 0.3) \times 10^{-3}$, respectively. For the isonicotinic acid complex, measurements at 250 and 285 nm gave $K_a = (4.9 \pm 0.2) \times 10^{-3}$ and $(4.4 \pm 0.6) \times 10^{-3}$, respectively.

Vanadium(II) solutions were prepared by reducing vanadyl perchlorate, $VO(ClO_4)_2$, solutions with amalgamated zinc. Solutions containing V^{2+} were maintained in an atmosphere of nitrogen in vessels stoppered with serum caps. Reaction mixtures were prepared in spectrophotometric cells. Reactions were begun by adding V^{2+} to the reaction mixture with a hypodermic syringe. The reactions were followed by means of absorbance measurements made on a Cary 14 recording spectrophotometer.



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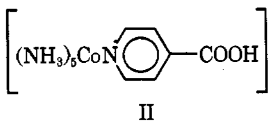

II

Results and Discussion

Cobalt(III) complexes I and II were found to react with V^{2+} to produce equimolar amounts of Co^{2+} and

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[1] F. R. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1162 (1968).

[2] (a) H. Taube and E. S. Gould, *Accounts Chem. Res.*, **2**, 321 (1969). (b) R. G. Gaunder and H. Taube, *Inorg. Chem.*, **9**, 2627 (1970).

[3] E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967.

V^{3+}. The kinetics of these reactions were studied at 25° and 1.0 M ionic strength and the reactions were found to be first order with respect to both Co(III) and V^{2+}. The observed second-order rate constants, k_{obsd}, appear in Tables I and II. For both reactions the rate constants depend upon $[H^+]$ according to a relation of the form

TABLE I
RATE CONSTANTS FOR THE REDUCTION OF (NICOTINIC ACID)PENTAAMMINECOBALT(III) BY $V^{2+\,a}$

$(H^+)_0$, M	k_{obsd},^{b} M^{-1} sec^{-1}	k_{calcd}, M^{-1} sec^{-1}	No. of runs
0.945	1.23 ± 0.06	1.29	4
0.730	1.32 ± 0.07	1.37	2
0.290	1.88 ± 0.05	1.82	2
0.243	2.13 ± 0.04	1.95	3
0.137	2.47 ± 0.04	2.52	3
0.075	3.33 ± 0.03	3.38	6
0.026	5.35 ± 0.02	5.33	2

[a] At 25° and 1.0 M ionic strength. [b] Error limits are the standard deviations.

TABLE II
RATE CONSTANTS FOR THE REDUCTION OF (ISONICOTINIC ACID)PENTAAMMINECOBALT(III) BY $V^{2+\,a}$

$(H^+)_0$, M	k_{obsd},^{b} M^{-1} sec^{-1}	k_{calcd}, M^{-1} sec^{-1}	No. of runs
0.946	2.29 ± 0.03	2.28	4
0.244	3.66 ± 0.07	3.71	2
0.136	4.52 ± 0.07	4.49	2
0.075	5.24 ± 0.19	5.23	4
0.022	6.22 ± 0.03	6.23	2

[a] At 25° and 1.0 M ionic strength. [b] Error limits are the standard deviations.

$$k_{obsd} = a + \frac{b}{c + (H^+)}$$

The values of a, b, and c are, respectively, 1.0 M^{-1} sec^{-1}, 0.25 sec^{-1}, and 0.035 M for the nicotinic acid complex and 1.4 M^{-1} sec^{-1}, 0.97 sec^{-1}, and 0.18 M for the isonicotinic acid complex.

A mechanism in which the dissociated and undissociated forms of I or II react with V^{2+} at different rates gives a rate law of the observed form (where complexes I or II are represented by $CoLH^{3+}$)

$$CoLH^{3+} = CoL^{2+} + H^+ \qquad K_a$$

$$CoLH^{3+} + V^{2+} \xrightarrow{k} \text{products}$$

$$CoL^{2+} + V^{2+} \xrightarrow{k'} \text{products}$$

$$k_{obsd} = \frac{k(H^+) + k'K_a}{K_a + (H^+)} = k + \frac{(k' - k)K_a}{K_a + (H^+)}$$

The acid dissociation constants, K_a, for complexes I and II are 0.0027 and 0.0047, respectively, at 25° and 1.0 M ionic strength. The complete lack of agreement between the values of c and the actual values of K_a rule out this mechanism for both complexes.

The observed rate equation can be interpreted by an alternate mechanism. In this case a arises from a simple bimolecular reaction of Co(III) with V^{2+} whereas the second term involves a Co^{III}–V^{2+} complex to which the steady-state approximation can be applied. The rate equation is consistent with either of two mechanisms[4] depending on whether proton loss precedes (mechanism I) or follows (mechanism II) formation of the $CoLV^{4+}$ intermediate.

mechanism I

$$CoLH^{3+} + V^{2+} \xrightarrow{k_0} \text{products}$$

$$CoLH^{3+} \rightleftharpoons CoL^{2+} + H^+ \qquad K_a$$

$$CoL^{2+} + V^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLV^{4+}$$

$$CoLV^{4+} + H^+ \xrightarrow{k_2} \text{products}$$

$$k_{obsd} = k_0 + \frac{k_1K_a}{(k_{-1}/k_2) + (H^+)}$$

mechanism II

$$CoLH^{3+} + V^{2+} \xrightarrow{k_0} \text{products}$$

$$CoLH^{3+} + V^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CoLV^{4+} + H^+$$

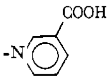
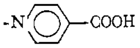
$$CoLV^{4+} \xrightarrow{k_4} \text{products}$$

$$k_{obsd} = k_0 + \frac{k_3k_4/k_{-3}}{(k_4/k_{-3}) + (H^+)}$$

For complex I we obtain $k_1 = b/K_a = 93$ M^{-1} sec^{-1} and $k_3 = b/c = 7.1$ M^{-1} sec^{-1}. Similarly for complex II, $k_1 = 200$ M^{-1} sec^{-1} and $k_3 = 5.3$ M^{-1} sec^{-1}. Rate constants k_1 and k_3 involve substitution on V^{2+}. Oxidation–reduction reactions which appear to be controlled by substitution on V^{2+} have rate constants between 8 and 30 M^{-1} sec^{-1} in cases where electrostatic and steric effects are small.[5] It is possible to rule out mechanism I since k_1 exceeds the specific rate of substitution on V^{2+}. Values of $k_3 = 7.1$ M^{-1} sec^{-1} and 5.3 M^{-1} sec^{-1} appear reasonable for the substitution of a neutral –COOH group since the other substitution-limited rate constants refer to the approach of a negative group.

Values of the kinetic parameters k_0, k_3, and k_4/k_{-3} (Table III) were obtained from the kinetic data using a nonlinear least-squares fitting program.[6] Calculated values of the second-order rate constants are listed in Tables I and II for comparison with the average values of k_{obsd}.

TABLE III
KINETIC PARAMETERS FOR THE REACTIONS OF $(NH_3)_5CoL^{3+}$ WITH $V^{2+\,a}$

L	k_0,M^{-1} sec^{-1}	k_3,M^{-1} sec^{-1}	k_4/k_{-3}, M
	1.0 ± 0.1	7.1 ± 0.6	0.035 ± 0.006
	1.4 ± 0.2	5.3 ± 0.2	0.18 ± 0.03

[a] Ionic strength 1.0 M and 25°.

The reaction of $Co(NH_3)_5py^{3+}$ with V^{2+} exhibits an acid-independent rate constant of 0.24 M^{-1} sec^{-1}. The lack of a suitable bridging group demands that this reaction is an outer-sphere process.

Cr^{2+} reduces nicotinamidepentaamminecobalt(III) ion ($k_{outer} = 1.4 \times 10^{-2}$ M^{-1} sec^{-1}) *via* an outer-sphere path about 3 times faster than $Co(NH_3)_5py^{3+}$ ($k = 4 \times 10^{-3}$ M^{-1} sec^{-1}).[1] Therefore we might expect V^{2+} to reduce I and II *via* an outer-sphere path several times faster

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(4) A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

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

(6) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963); IBM Share Program SDA No. 3094 (1964).

than it reduces $\mathrm{Co(NH_3)_5py^{3+}}$. It appears that an outer-sphere process may account for all or a substantial portion of the k_0 path for I and II.

It is apparent that especially at low acid concentrations a substantial part of the reaction proceeds through an inner-sphere activated complex. It is of interest to compare these inner-sphere processes for $\mathrm{V^{2+}}$ to other inner-sphere reactions in which 3- and 4-substituted pyridines act as bridging ligands.

The reductions of the N-coordinated pyridinecarboxylic acid complexes by $\mathrm{Cr^{2+}}$ proceed in part by paths with inverse dependence upon $(\mathrm{H^+})$. The paths make a contribution to the observed rate equal to $0.015(\mathrm{H^+})^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$ and $\leq 0.03(\mathrm{H^+})^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$ for the reaction of $\mathrm{Cr^{2+}}$ with I and II, respectively.[7] These may be compared with $0.25(\mathrm{H^+})^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$ and $0.97(\mathrm{H^+})^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$ for the corresponding reductions by $\mathrm{V^{2+}}$. The latter values are equal to k_3k_4/k_{-3} which would be the specific rates if substitution on $\mathrm{V^{2+}}$ were rapid.

It has been proposed[2] that the $\mathrm{Cr^{2+}}$ reduction of isonicotinamidepentaammineruthenium(III) proceeds by a resonance-transfer mechanism[8] in which the electron is transferred directly to the ruthenium(III) acceptor orbital. Ru(III) complexes are reduced much more rapidly by $\mathrm{Cr^{2+}}$ than the corresponding Co(III) complexes. Presumably this is due to symmetry matching of Ru(III) (a π acceptor) but not Co(III) (a σ acceptor) with the π-bridging ligand. Other studies[1] indicate that the isonicotinamidepentaamminecobalt(III) ion reacts with $\mathrm{Cr^{2+}}$ by a stepwise mechanism.[2]

A resonance-transfer mechanism is indicated for the $\mathrm{V^{2+}}$ reactions of this study because the effect of symmetry matching of the donor with the π-bridging ligand is evident. Thus $\mathrm{V^{2+}}$, a weaker reductant but a π donor, reacts more rapidly than $\mathrm{Cr^{2+}}$ (a σ donor) with both of the Co(III) complexes.[9-11] Similar conclusions have been reached for the $\mathrm{V^{2+}}$ reductions of $\mathrm{CrOAc^{2+}}$ [12] and $\mathrm{Co(NH_3)_5ox^{2+}}$.[10]

It is of interest to note that the rate of $\mathrm{V^{2+}}$ reduction (by the inverse acid path) of the isonicotinate complex is only about 4 times greater than that of the nicotinate complex. Because resonance effects are transmitted between para positions much more effectively than between meta positions, a larger factor would be expected. Thus the effectiveness of the bridging ligands in this study is not strongly dependent upon the π interaction they provide between the metal ions. Apparently the interaction between the donor and acceptor orbitals is great enough so that the probability of transfer during the lifetime of the energy-matched intermediate is near unity; *i.e.*, the process is adiabatic.

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(7) F. R. Nordmeyer, work in progress.

(8) J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

(9) A greater rate for $\mathrm{V^{2+}}$ would not be inconsistent with a stepwise process if electron transfer to the ligand were rate determining. However, this seems unlikely to us for two reasons: (1) electron transfer to the 3-substituted pyridine should be many times slower than to the more easily reduced 4-substituted system, whereas the corresponding complexes are reduced at similar rates (within a factor of 4); (2) $\mathrm{Cr^{2+}}$ is generally more reactive than $\mathrm{V^{2+}}$ in reducing unsaturated organic carboxylic acids.[10,11] This suggests that electron transfer to unsaturated systems is faster for $\mathrm{Cr^{2+}}$ than $\mathrm{V^{2+}}$, but since the mechanisms of the organic reductions are unknown, this conclusion is uncertain.

(10) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(11) E. Vrachnou-Astra and D. Katakis, *J. Amer. Chem. Soc.*, **89**, 6772 (1967); A. Malliaris and K. Katakis, *ibid.*, **87**, 3077 (1965).

(12) E. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

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Stereoselectivity in Octahedral Complexes. IV.[1] Separation and Identification of the Diastereomers of Tris[(+)-3-acetylcamphorato]cobalt(III) and -chromium(III)

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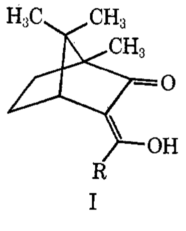
The four possible diastereomers of tris[(+)-3-acetylcamphorato]cobalt(III) and of tris[(+)-3-acetylcamphorato]chromium(III) have been separated by preparative thin layer chromatography on silica gel. Absolute configurations are assigned to the individual isomers of the Co(III) complex based on CD and pmr spectra. Certain of the Cr(III) and Co(III) diastereomers are shown to be isomorphous using X-ray powder diffraction data. Assuming the isomorphous isomers have the same absolute configurations, configurations are assigned to the individual Cr(III) diastereomers. CD spectra of Cr(III) and Co(III) diastereomers assigned the same configuration are qualitatively very similar. Relative isomer abundances for each complex are qualitatively the same; the Λ-trans isomer is most abundant for both metals. Kinetic control of stereoselectivity is maintained for the Cr(III) complex and apparently to some extent for the Co(III) complex.

Introduction

Camphor is readily available in high optical purity and is easily converted into bidentate β-keto enolate ligands such as hydroxymethylenecamphor, hmcH (I, R = H), or acetylcamphor, atcH (I, $\mathrm{R = CH_3}$). The



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[1] Part III: K. S. Finney and G. W. Everett, Jr., *Inorg. Chem.*, **9**, 2540 (1970).