(III)–ammine complexes can presently be offered. Despite this disturbing aspect it is of interest to note that an outer-sphere path is observed for the protonated forms of all complexes. In addition, inner-sphere type mechanisms appear to occur also in all cases with attack of the reductant at the remote carboxylic group (protonated or unprotonated) and intramolecular transfer of an electron within cobalt(III)–vanadium(II) intermediates (in a protonated or deprotonated form).

Electron transfer through extended organic bridging ligands with $[Cr(OH_2)_6]^{2+}$ as reductant is observed (a) if the uncomplexed organic ligand is reducible by Cr(II) and (b) if conjugation from the electron donor to the acceptor is given.[15] We propose that the same conditions also apply for the reductions of binuclear cobalt(III)–ammine complexes with V(II) as reductant. Fumaric acid and maleic acid[16] as well as acetylenedicarboxylic acid are reducible by V(II) and have good conjugation. Other data from Table II are in line with this interpretation. For the reduction of the μ-malonato complex by V(II) only an outer-sphere mechanism is detected[17] due to the lack of conjugation whereas the μ-terephthalato complex is reduced via an outer-sphere mechanism because of its irreducibility.[18] There appears to be only one serious exception to this scheme. The nonreducible pyridine-3-carboxylic acid is reported to function as an electron-mediating ligand when the N-coordinated (pyridine-3-carboxylato)-pentaamminecobalt(III) complex is reduced by V(II).[2] The pyridine-4-carboxylato analogue on the other hand fits.

For reasons not yet understood the protonated forms of I and II are reduced by V(II) via outer-sphere mechanisms—when $[Cr(OH_2)_6]^{2+}$ is the reductant inner-sphere paths are observed.[5,6] Compared with Cr(II) [V-$(H_2O)_6]^{2+}$ is a much weaker reductant. This may account for a pronounced selectivity of V(II) regarding its capability to

function as an inner-sphere reagent with attack at a remote polar group of the organic bridging ligand. Protonation of the remote carboxylic group may affect the lowest unoccupied antibonding orbital of I and II to such a degree that an inner-sphere path becomes energetically unfavorable. This interpretation is somewhat vitiated by the observation that the protonated form of I is reduced more rapidly than the unprotonated form if $[Cr(H_2O)_6]^{2+}$ is the reductant.[6]

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Kinetic and Electron Spin Resonance Spectroscopic Evidence for a Chemical Mechanism in the Chromium(II) Reduction of Two (Pyrazinecarboxylato)amminecobalt(III) Complexes
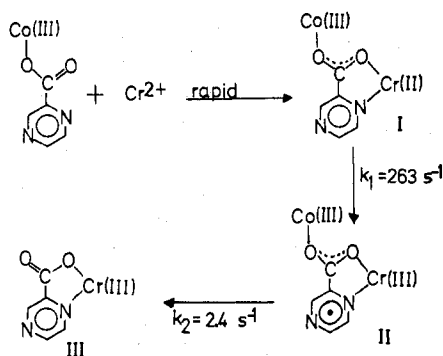
HANS SPIECKER and KARL WIEGHARDT*

The reductions of the mononuclear complex (pyrazinecarboxylato)pentaamminecobalt(III) (A) and the binuclear complex μ-pyrazinecarboxylato(O,O')-di-μ-hydroxo-bis[triamminecobalt(III)] (B) by $Cr(H_2O)_6^{2+}$ have been studied. Kinetic and ESR spectroscopic measurements indicate the formation of transient radical species. Direct evidence for the occurrence of a chemical mechanism has been obtained for the Cr^{2+} reduction of complex A.

Inner-sphere electron transfer between two metal ions in solution is effected by means of a bridging ligand which is coordinated to both metal centers in the precursor complex. The bridging ligand can help to increase the probability of electron transfer by tunneling ("resonance transfer"), or the ligand can accept an electron, generating a radical intermediate, and in a subsequent step the electron is passed onto the oxidant center ("chemical, radical or two-step mechanism").[1-3] Assignment of the latter mechanism for the Cr^{2+} reduction of Co(III) and Cr(III) complexes via the same organic bridging ligand is based mainly on indirect criteria such as comparison of rates.[4]

In 1972 Gould reported the spectrophotometric detection of a reactive, strongly absorbing intermediate in the Cr^{2+} reduction of the (pyrazinecarboxylato)pentaamminecobalt(III) complex (A).[5] From the kinetic behavior of the formation and subsequent decay of this transient species he assigned structure II (see Scheme I) in which the electron is located on the organic ligand.

We have studied the kinetics of the Cr^{2+} reduction of the binuclear μ-pyrazinecarboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complex (B). Reduction of the first Co(III) center should occur with remote attack of the reductant at either of the two heterocyclic nitrogen atoms, but

Scheme I

contrary to the mononuclear complex (A), no chelated precursor complex can be formed since both oxygen atoms of the carboxylic group are coordinated to two Co(III) ions.[6,12]
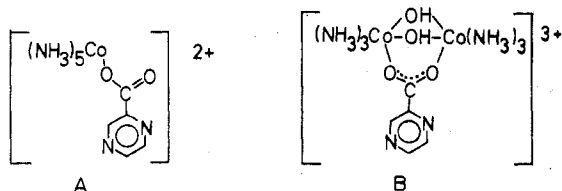
Experimental Section

Complexes. The mononuclear complex (pyrazinecarboxylato)-pentaamminecobalt(III) (A) was prepared from aquopentaamminecobalt(III) and the organic ligand in water as described in the literature.[7] The complex has a maximum of absorption at 502 nm (ϵ 75 L mol^{-1} cm^{-1}) in good agreement with previous values. The binuclear complex μ-pyrazinecarboxylato(O,O')-di-μ-hydroxo-bis[triamminecobalt(III)] perchlorate (B) was prepared by a modified method described previously for the synthesis of binuclear carboxylato complexes.[8] To a solution of 1.2 g of pyrazinecarboxylic acid in 40 mL of 0.25 M perchloric acid and 10 mL of dioxane at 55 °C 6 g of tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate dihydrate[9] was added in small amounts with stirring. The temperature was maintained for 15 min, during which most of the dioxane was evaporated by bubbling a stream of nitrogen through the solution. To the cooled (5 °C) solution 10 mL of concentrated perchloric acid and 15 g of solid NaClO$_4$ were added. The mixture was kept at 0 °C for 12 h. Red crystals were collected and washed with ethanol and diethyl ether. Anal. Calcd for [(NH$_3$)$_3$Co(OH)(OH)(C$_5$H$_4$N$_2$)Co(NH$_3$)$_3$]-(ClO$_4$)$_4$·H$_2$O: C, 7.6; H, 3.3; NH$_3$, 12.9; Cl, 17.9. Found: C, 7.8; H, 3.3; NH$_3$, 12.6; Cl, 17.8. The UV–visible spectrum had a maximum at 524 nm (ϵ 110 L mol^{-1} cm^{-1}), a shoulder at 298 nm (ϵ 390 L mol^{-1} cm^{-1}), and a maximum at 270 nm (ϵ 15.5 × 10^3 L mol^{-1} cm^{-1}).

Reagents. Solutions of the Cr(H$_2$O)$_6$$^{2+}$ ion in perchloric acid were prepared by electrolytic reduction of chromium(III) under an argon atmosphere. Lithium perchlorate was obtained from Li$_2$CO$_3$ and concentrated HClO$_4$ and was purified by recrystallization.

Physical Measurements. Kinetic runs were followed on a Durrum stopped-flow spectrophotometer at the first absorption maxima of the complexes (502 nm for complex A and 524 nm for complex B) at 25 °C. Chromium concentrations were determined spectrophotometrically as chromate (λ 372 nm, ϵ 4.8 × 10^3 L mol^{-1} cm^{-1}), and solutions of cobalt(II), as CoCl$_4$$^{2-}$ or CoCl$_3$(H$_2$O)$^-$ by standard procedure. An apparent protonation constant, K, was determined spectrophotometrically for complex B at 2.0 M ionic strength (LiClO$_4$) and 25 °C. The largest difference in the spectra as a function of [H$^+$] was observed at 290 nm. Since complex B is a strong acid, it was not possible to obtain reproducible values for K at 1.0 M ionic strength.

The ESR spectra were obtained on a Varian V-4500 spectrometer equipped with an AEG NMR magnetic field oscillator. The g factors have been determined via the relation $g = 714.47\nu/H$ [ν is the klystron frequency (GHz); H is the strength of the magnetic field (G)]. Continuous-flow experiments of the reactants through the flat ESR cell were carried out with aqueous perchlorate solutions ([H$^+$] = 0.1 M) of 0.024 M complex A and 0.012 M Cr(H$_2$O)$_6$$^{2+}$ at 20 °C.

Determination of Products. Product analyses of reaction products were carried out by cation-exchange chromatography at 2 °C using

**Table I.** Visible Absorption Spectra of Cr(III) Products Obtained from Ion-Exchange Separations

Complex	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}	Ref
III	548	35	400 sh	50	This work
IX^a	564	25	400 sh		This work
XII^a	566	28	408	29	11
XIII	551	35			11
Cr(H$_2$O)$_5$OAc^{2+}	570	24	410	22	19
Cr(H$_2$O)$_6$$^{3+}$	571	13.2	408	15.5	19

^{a} Extinction coefficients are average values per chromium atom.

the resin Sephadex SP C-25 in the H$^+$ form in order to obtain the visible absorption spectra of the separated Cr(III) products. Separation of 1:1 mixtures of the mononuclear complex (A) and Cr(H$_2$O)$_6$$^{2+}$ using a 10% excess of reductant (in a typical experiment [Cr^{2+}] = 4.4 × 10^{-3} M, [Co^{3+}] = 4.0 × 10^{-3} M, and [H$^+$] = 0.1 M) yielded only two fractions: a pink band containing 75% of the initial chromium and Co(H$_2$O)$_6$$^{2+}$ (98% of the initial cobalt(III)) and a blue-violet band which was identified by its spectrum as Cr(H$_2$O)$_6$$^{3+}$ (20–25% of the initial chromium). The pink Cr(III) complex has an apparent charge of 2+. This is consistent with the previously assigned structure III. The visible absorption maxima of this species are listed in Table I; they are not in agreement with previous values.[10] After mixing of the two reactants, the color of the reaction mixture was green but faded to normal pink upon addition of oxygen or dilution with H$_2$O. We did not observe the precipitation of a "rust-colored" material.[10] In a separate experiment we demonstrated qualitatively that reaction of complex III with excess Cr^{2+} causes the formation of a green pigment.

Separation of 1:2 reaction mixtures (2 °C) of the binuclear complex (B) and Cr^{2+} (10% excess) yielded three fractions (in a typical experiment [Cr^{2+}] = 2.2 × 10^{-3} M, [Co$^{III}_2$] = 1.0 × 10^{-3} M, and [H$^+$] = 0.1 M): a pink band which was eluted off the column with 0.1 M HClO$_4$ containing Co(H$_2$O)$_6$$^{2+}$ (97%) and the chelated complex III (10% of the initial chromium), a blue-violet band of Cr(H$_2$O)$_6$$^{3+}$ (25%) using 0.25 M HClO$_4$, and, finally, on eluting with 1.0 M HClO$_4$, a third blue-gray band which was slowly recovered off the column (65% Cr(III)). This species has an apparent charge >3+. The visible maxima are listed in Table I. A very strong absorption <350 nm is due to coordinated pyrazinecarboxylic acid. Therefore, it is concluded that a binuclear chromium(III) complex containing a pyrazinecarboxylato bridging ligand is formed. The product distribution was shown to be the same when 1:1 mixtures (1 mol of complex B and 1 mol of Cr^{2+}) were reacted, but here the unreacted binuclear complex (B) (50%) with a 3+ charge was eluted off the column in the second fraction, together with Cr(H$_2$O)$_6$$^{3+}$. In this case 85% of initial chromium was recovered from the third fraction and only 5% of the chelated complex III. This implies that the binuclear Cr(III) complex is a genuine primary product of the reaction. Again it was shown that solutions containing only the binuclear Cr(III) species react extremely rapidly with Cr^{2+} to give green solutions.

There are at least three structures—IX (see Scheme II), X, and
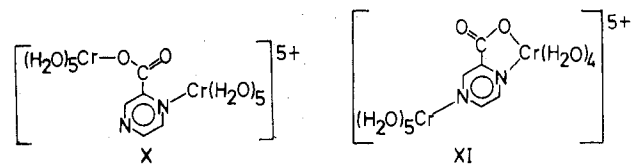
XI—conceivable for the binuclear Cr(III) complex if it is assumed that reduction of the first Co(III) center of B occurs via remote attack of Cr^{2+} at one of the heterocyclic nitrogen atoms and reduction of the Co^{III}–Cr^{III} intermediate (e.g., VI in Scheme II) occurs via adjacent attack with or without chelation at the adjacent carboxylic group. A tentative assignment of structure IX is based on the similarity of the visible spectra of complex XII. (For steric reasons a chelated
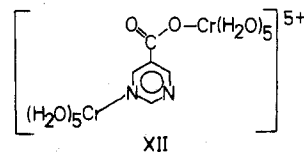
Scheme II
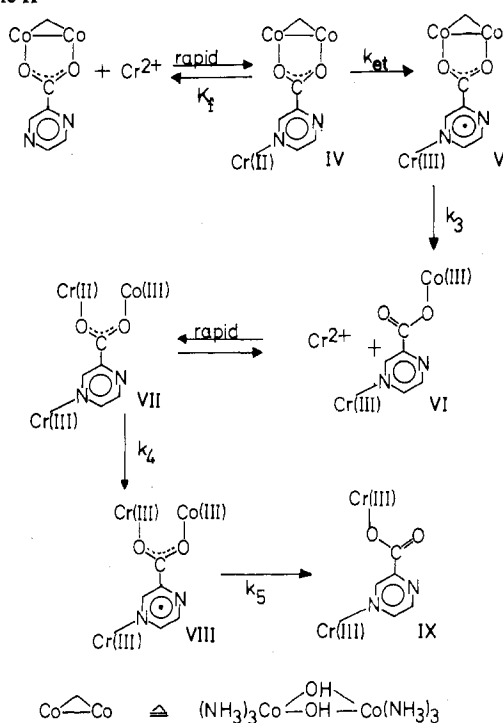
structure—an analogue of XI—cannot be formed during the course of the Cr^{2+} reduction of the μ-5-pyrimidinecarboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complex.[11] In addition, the spectra of III (Scheme I) and XIII which contain N-coordinated organic
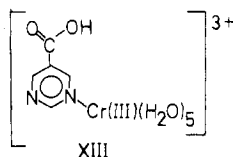
ligands are very similar and exhibit larger extinction coefficients (35) than O-coordinated carboxylatopentaaquochromium(III) complexes (24 or less). The observed value for the binuclear Cr(III)species (25) is considered to be more characteristic for structure IX or X. An extinction coefficient of 30–35 per chromium atom would be expected for structure XI where both chromium atoms are N-coordinated. Furthermore, the position of the absorption maximum of N-coordinated (H$_2$O)$_5$Cr^{III} species is shifted 15–25 nm to lower wavelengths as compared to O-coordinated species. Therefore, structure XI would be expected to show a maximum at 550 nm (e.g., structures III and XIII). The observed value of 566 nm is intermediate between O-coordinated ($\sim$570 nm) and N-coordinated ($\sim$550 nm) (H$_2$O)$_5$Cr^{III} species.

Cr^{2+} Reduction of Complex B. The stoichiometry of the reduction of complex B by Cr^{2+} was shown to be 2:1 from ion-exchange experiments as in (1) when the complex was in excess (20%) over the

$$2Cr^{2+} + Co^{III}{}_2 \rightarrow 2Cr(III) + 2Co^{2+} \quad (1)$$

reductant. When Cr^{2+} is in excess, a deep green pigment is formed very rapidly, in addition to Co(II) and Cr(III).

Stopped-flow traces of 2:1 reaction mixtures (2 mol of reductant and 1 mol of complex B) and traces with the oxidant in excess (1:1.13) show four distinct stages of the reaction at λ 524 nm: (1) a rapid increase in absorbance followed by (2) a slight decrease which again is followed by (3) a slight increase in absorbance and (4) a large decrease (Figure 1a and b). This is interpreted as in Scheme II: the formation of two different radical cations V and VIII causes increases in absorbance, whereas the formation of intermediate VI and the final binuclear chromium(III) complex IX is accompanied by decreases in absorbance.

Stopped-flow traces of reaction mixtures using pseudo-first-order conditions with Cr^{2+} in at least tenfold excess over complex B revealed only two stages: a marked increase in absorbance which is followed by a second smaller increase (Figure 1c). The kinetics of formation
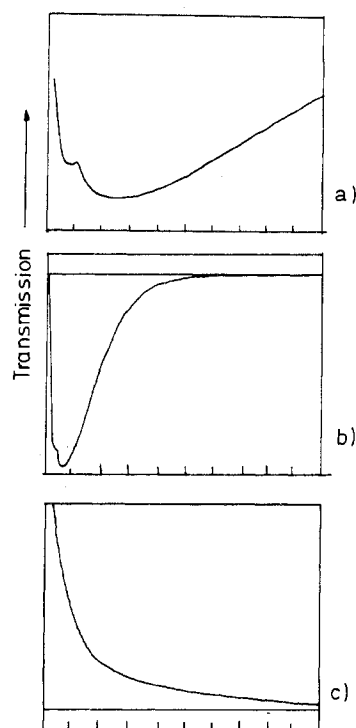

Figure 1. Oscilloscope traces for the reaction of μ-pyrazine-carboxylato(O,O')-di-μ-hydroxo-bis[triammine cobalt(III)] with Cr^{2+} at 25 °C (λ 524 nm). Four stages of the reaction are illustrated in parts a and b with different time bases: (a) 0.01 s/division; (b) 0.05 s/division. Complex B is in excess over Cr^{2+}. Only two stages of the reaction observed using excess Cr^{2+} are demonstrated in part c (time base 0.01 s/division). Conditions: (a) [Cr^{2+}] = 4.0 × 10^{-3} M, [Co$^{III}{}_2$] = 2.1 × 10^{-3} M, [H$^+$] = 1.0 M; (b) [Cr^{2+}] = 4.0 × 10^{-3} M, [Co$^{III}{}_2$] = 4.5 × 10^{-3} M, [H$^+$] = 0.1 M; (c) [Cr^{2+}] = 1.1 × 10^{-2} M, [Co$^{III}{}_2$] = 5 × 10^{-4} M, [H$^+$] = 0.05 M.

of these first and second strongly absorbing species were measured from such traces applying a standard consecutive reaction treatment. The formation of the first strongly absorbing species is accelarated at high [H$^+$] (0.01–0.70 M), is strictly first order in [Cr^{2+}] (0.01–0.085 M), and follows the rate law
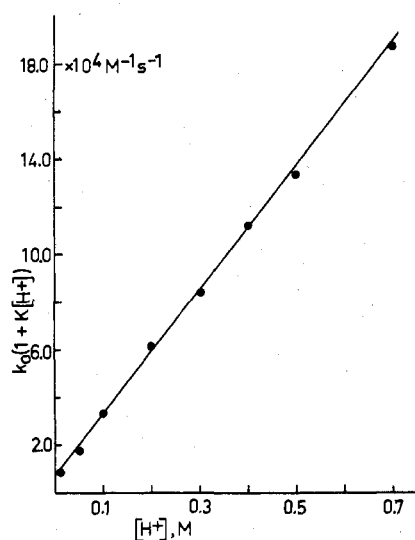
$$\text{rate} = k_0 [Cr^{2+}][\text{complex B}]$$

$$k_0 = \frac{k_a K[H^+] + k_b}{1 + K[H^+]} \quad (2)$$

This is consistent with both the protonated (k_a) and deprotonated (k_b) forms of complex B reacting to form the radical cation V (K is the equilibrium constant for the protonation). Second-order rate constants, k_0 (M^{-1} s^{-1}), are listed in Table II. As shown in Figure 2, good linear behavior of $k_0(1 + K[H^+])$ with [H$^+$] was found using a value of 1.5 M^{-1} for K at 25 °C. This value is not very accurate since formation of radical V is in some cases complete to 70% during mixing time ($\sim$3 ms). Therefore, we feel that the spectrophotometrically determined value of K = 0.45 ± 0.2 M^{-1} at 25 °C and ionic strength 2.0 M (LiClO$_4$) does not contradict the above interpretation. Values of k_a = (1.72 ± 0.02) × 10^5 M^{-1} s^{-1} and k_b = (6.6 ± 1.0) × 10^3 M^{-1} s^{-1} at 25 °C (μ = 1.0 M (LiClO$_4$)) were evaluated from the slope ($k_a K$) and intercept (k_b) of the straight line (Figure 2) which was obtained from a linear least-squares program in which each data point was given equal weighting.

The rate of formation of the second strongly absorbing species which is only generated when excess Cr^{2+} is present (increase in absorbance is followed vs. time; Figure 1c) was found to be independent of [Cr^{2+}] (0.006–0.085 M) and [H$^+$] (0.01–0.7 M) (Table II): k_5 = 24 ± 1 s^{-1} at 25 °C and μ = 1.0 M (LiClO$_4$). This is in excellent agreement with results obtained from oscilloscope traces (Figure 1b) for the last step of the reaction (now a strong decrease in absorbance is observed) applying second-order conditions (25% excess of oxidant over reductant). Plots of log ($A_t - A_\infty$) vs. time were linear after 1 half-life indicating a first-order process which is independent of [H$^+$] and

Table II. Kinetic Data for the First and Last Stages of the Cr^{2+} Reduction of Complex B at 25 °C and μ = 1.0 M (LiClO$_4$)
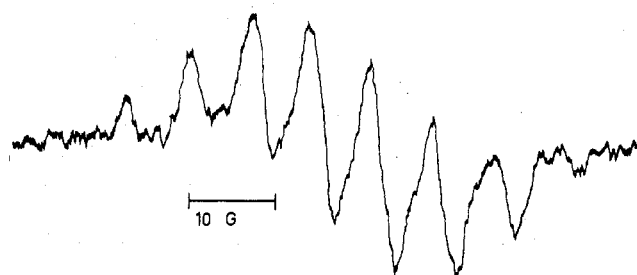
[H$^+$], M	10^2[Cr^{2+}], M	10^4[(Co$^{III}_2$)], M	$10^{-3}k_0$, M^{-1} s^{-1}	k_s, s^{-1}
(a) Pseudo-First-Order Conditions (Excess Reductant)				
0.01	0.99	1.0	8.0	24.5
0.05	0.62	5.0	15.8	24.6
0.05	1.07	5.0	17.5	24.3
0.05	3.05	5.0	14.1	24.7
0.05	5.02	5.0	14.0	24.0
0.05	7.11	5.0	14.2	24.1
0.05	8.50	5.0	15.1	25.3
0.10	1.03	1.0	28.6	25.0
0.10	1.03	5.0	28.7	23.5
0.20	0.99	5.0	46.8	24.4
0.30	0.97	5.0	57.9	26.0
0.40	1.07	5.0	69.3	23.8
0.50	1.02	5.0	76.0	24.0
0.70	0.99	5.0	91.0	24.3
(b) Second-Order Conditions				
0.10	0.40	25.0		21.2
1.00	0.40	50		23.2

Figure 3. Transient ESR spectrum of the reaction of complex A (large excess) and Cr(H$_2$O)$_6^{2+}$ at 20 °C (continuous flow of reactants through the flat ESR cell).

An almost identical transient ESR spectrum as in Figure 3 is observed when aqueous solutions of uncomplexed pyrazinecarboxylic acid and Cr^{2+} are mixed in a continuous flow. An intermediate yellow color is formed immediately after mixing which becomes intensively green. This behavior is paralleled by qualitative stopped-flow experiments. Upon mixing reactant solutions ([pyrazinecarboxylic acid] $= 1 \times 10^{-3}$ M and [Cr^{2+}] $= 0.01$ M in 0.2 M perchloric acid, 25 °C) a marked increase in absorbance at λ 524 nm during the first 10 ms is observed which is followed by a rapid decrease in absorbance (0.1 s). The ESR signal disappears rapidly when the flow is stopped. The green pigment does not exhibit an ESR signal. It is suggested that the green material is a subsequent reaction product of the intermediate yellow radical XIV. It is noted that these green pigments display
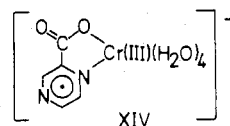
the chemistry characteristic of one-electron reductants,[10] and the lack of detectable ESR signals does not necessarily mean that the green pigments are not radical species.[20]

Discussion

The first rapid stage of the Cr^{2+} reduction of complex B which is observed as a large increase in absorbance during the first 0.01 s after mixing can be assigned to the formation (k_0) of a mixed Cr(III)–Co(III) radical cation V (Scheme II). This assignment is supported by the rate law (2). The irreversible formation of a chelated complex I via adjacent attack with chelation of Cr^{2+} is very rapid (Scheme I). Therefore, the subsequent transformation I → II would be independent of [Cr^{2+}] and [H$^+$].[5] If both oxygen atoms of the carboxylic group of the organic ligand are already coordinated to two Co(III) centers as in complex B a chelated Cr(II) complex cannot be formed.[6,12] Only the reversible binding of Cr^{2+} at one of the remote heterocyclic nitrogen atoms is possible. The observed first-order dependence on [Cr^{2+}] for the formation of V is consistent with this interpretation: the measured rates are a function of the formation constant of IV (Scheme II), K_f, and the intrinsic electron-transfer rate constant, k_{et}

$$k_0 = k_{et}K_f \qquad (3)$$

It has not been possible to establish which of the two heterocyclic nitrogens is the actual point of attack of the reductant. The nitrogen ortho to the carboxylic group may be less accessible due to steric hindrance. Therefore, in Scheme II the nitrogen in the meta position is considered to be the more likely site of attack for the first Cr^{2+}.

A further interesting facet is the dependence of the rate of formation of V on [H$^+$]. Despite an increased positive charge which affects the formation constant, K_f, unfavorably, the protonated form of complex B reacts more rapidly (k_a = 1.72 $\times$ 10^5 M^{-1} s^{-1}, 25 °C) to form the radical cation V than the unprotonated form (k_b = 6.6 $\times$ 10^3 M^{-1} s^{-1}). This may reflect a purely electrostatic effect, since the additional positive charge on the heterocyclic ring could "pull" an electron onto the ring

Figure 2. Dependence of k_0 on [H$^+$] for the first step of the Cr^{2+} reduction of complex B at 25 °C, μ = 1.0 M (LiClO$_4$), and a protonation constant of K = 1.5 M^{-1} (calculated from kinetic data).

[Cr^{2+}]. The activation parameters for this first-order process were determined: $\Delta H_5^{\ddagger}$ = 13.9 $\pm$ 0.1 kcal mol^{-1}, $\Delta S_5^{\ddagger}$ = −5.4 $\pm$ 0.4 cal K^{-1} mol^{-1} (Scheme II).

ESR Measurements. Upon mixing of solutions containing the oxidant A and Cr^{2+} (complex A is held in large excess over the reductant in order to avoid the formation of the green pigment) in a continuous flow a transient ESR spectrum shown in Figure 3 is observed. This signal disappears when the flow is stopped within ~2 s. *No* such spectrum is observed using identical experimental conditions (a) when either of the reactants is passed separately through the flat ESR cell, (b) when a solution containing only the final reaction products is in the cell, and (c) when the green pigment is studied which was generated in separate experiment with excess Cr^{2+} over the oxidant. A g factor of 2.003 076 indicates that the unpaired electron is located largely on the organic ligand. Therefore, the ESR spectrum is regarded as direct evidence that the radical cation II is formed during the Cr^{2+} reduction of the cobalt(III) center in complex A. It is noted that the kinetic data of Scheme I which were obtained using excess Cr^{2+} almost certainly do not correspond to the formation and decay of the radical II.[20] Due to the small concentration of the transient radical under our experimental conditions it has not been possible to obtain a better resolution of the ESR spectrum.

No such transient ESR spectrum was observed under our experimental conditions when solutions of complex B and Cr^{2+} were mixed.

which has less electron density if it is protonated.

The decay of the proposed radical cation VIII is an *intramolecular* electron-transfer process. The small negative activation entropy (-5.4 cal K^{-1} mol^{-1}) can be regarded as further evidence that the large negative values of the entropy of activation which are observed for inner-sphere redox reactions of $Cr(H_2O)_6{}^{2+}$ with mononuclear[14] and binuclear[15] carboxylatocobalt(III)–ammine complexes are the result of concentrating the charge (2+, 2+ or 2+, 3+) in the dielectric medium as has been pointed out by Taube et al.[16]

The intrinsic reducibility of the aromatic, heterocyclic carboxylic acid appears to be the driving force for the rapid formation of relatively stable radical species, since they are generated when the unbound ligand as well as complexes A and B are reacted with Cr^{2+}. The stability of the Co(III)–Cr(III) radical cations II and VIII may at least in part be due to a low "electron permeability" of the carboxylato group.[18] This has been discussed previously for the relative stable radical cation formed by the reaction of Co^{III}-$(NH_3)_5(O_2C-C_6H_4-NO_2-p)^{2+}$ with the hydrated electron.[17]

References and Notes

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Crystal Circular Dichroism Spectra of the Tris(ethylenediamine)cobalt(III) Chromophore. Direct Measurement of Transitions to Both E and A₂ Excited Levels

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Crystal circular dichroism spectra of the $\Lambda(+)_D$-tris(ethylenediamine)cobalt(III) chromophore diluted in a host crystal of racemic $2[Ir(en)_3]Cl_3\cdot NaCl\cdot 6H_2O$ were measured with light propagating both parallel and perpendicular to the threefold axis of the chromophore. The validity of the theoretical prediction that the trigonal components of the $A_{1g} \rightarrow T_{1g}$ octahedral transition ($A_1 \rightarrow E$ and $A_1 \rightarrow A_2$) contribute to the rotatory strength with approximately the same absolute value, but opposite signs, is demonstrated experimentally, thus supporting the interpretation of the solution spectra as being residual wing absorptions arising from extensive cancelation of the rotatory strengths of these two transitions.

Introduction

Optically active tris(diamine)cobalt(III) complexes usually exhibit two circular dichroism (CD) bands of opposite signs in the absorption region around 21 000 cm^{-1}. These bands are normally considered to correspond to transitions to the $E(D_3)$ and $A_2(D_3)$ excited levels of $T_{1g}(O_h)$ parentage in a D_3 environment, although there has been some disagreement in the literature about these assignments. McCaffery and Mason,[4] Schäffer,[5] and Kuroda and Saito[6] consider the solution spectra of the $\Lambda(+)_D$-$[Co(en)_3]^{3+}$ chromophore to correspond to residual wing absorptions resulting from extensive cancelation of the rotatory strengths of the two transitions, since the trigonal splitting is small. This argument is based on the assumption that solid-state and solution CD have the same physical cause, i.e., derive from a molecular property which is not greatly affected by the environment of the complex ion. Support for this assumption was provided several years ago by McCaffery et al.,[7] who compared solution and microcrystalline (KBr disks) CD spectra. Woldbye[8] and Dingle and

Ballhausen,[9] however, have argued that in contrast to the situation in the crystal, the complex ion may exist in two conformers in solution, so that the negative component in the solution spectrum of $\Lambda(+)_D$-$[Co(en)_3]^{3+}$ could be due to the presence of conformations of the chelate rings in solution which differ from those occurring in the crystal. However, the discussion given by Hawkins,[10] the results of Piper and Karipides,[11] Sudmeier et al.,[12] and Harnung et al.,[13] and the calculations of Stickland and Richardson[14] provide good grounds for regarding the solution CD spectra of $[Co(1,2$-diamine)$_3]^{3+}$ in general as being due to residual wing absorptions. It was demonstrated by these authors that there are only minor differences between the CD spectra of the lel$_3$ and lel$_2$ob conformers which occur in solution and that lel$_3$, the crystal conformer, shows two components in the CD spectrum. This means that results obtained for the solid phase may be directly related to solution and vice versa.

One of the difficulties encountered in attempts to resolve the controversy outlined above has been the fact that until very