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Outer-Sphere Electron-Transfer Reactions of Binuclear Complexes of Cobalt(III): Assessment of an Inductive Effect on the Rates. A Linear Relationship between the Selectivity of Redox Reactions and the Reduction Potentials of the Reductants

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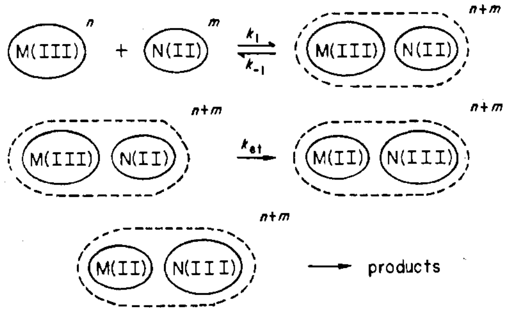
The kinetics of the outer-sphere reductions of a series of binuclear μ-(carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)] cations (carboxylate, formate, acetate, mono-, di-, or trifluoroacetate) by various reductants {$[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Ru(NH_3)_6]^{2+}$, $[Ti(dipic)_2]^-$, $[Fe(dipic)_2]^{2-}$ (dipic = pyridine-2,6-dicarboxylate)} have been measured at 25 °C. The logarithms of the second-order rate constants [$k_{x,y} = k_{et}^{x,y}K_0$ (M^{-1} s^{-1}) where K_0 = ion-pair association or encounter complex formation constant and $k_{et}^{x,y}$ = intramolecular electron-transfer rate constant] vary linearly with Taft's inductive parameter, σ_I, for substituents of the coordinated carboxylate groups (CH_3, H, CH_2F, CHF_2, CF_3), indicating an inductive effect on the intramolecular electron-transfer rates. $k_{CF_3,y} > k_{CHF_2,y} > k_{CH_2F,y} > k_{H,y} > k_{CH_3,y}$ is the order of decreasing reactivity observed for each reductant y used, irrespective of the charge of the reductant (2+, 1−, 2−). This is interpreted in terms of an increasing oxidizing ability of the Co(III) centers with increasing electron-withdrawing capability of the substituents. The selectivities of outer-sphere reductions of the μ-(trifluoroacetato) and of the μ-acetato complexes by a common reductant y (log $k_{CF_3,y}$ − log $k_{CH_3,y}$) are shown to be linearly correlated with the half-wave potential of the reductant y. The stronger the reductant y (i.e., more negative reduction potential) the smaller is the observed selectivity. Linear correlations exist between values of log $k_{x,y}$ for outer-sphere reductions of the series of μ-(acetato)-dicobalt(III) complexes, x, by two different reductants, y1 and y2, respectively: $\log k_{x,y1} = \alpha \log k_{x,y2} + \beta$. The slope α is shown to be most probably a linear function of the difference of the reduction potentials of the involved reductants y1 and y2: $\alpha = -(0.8 \pm 0.1)|E_0^{y1} - E_0^{y2}| + (1.00 \pm 0.04)$.

Introduction

The reaction sequence eq 1–3 describes the outer-sphere



(1)

(2)

(3)

electron-transfer process between two transition-metal complexes in solution.[1] The reactants form an ion pair (M(III) and N(II) have opposite charges) or an encounter complex (like-charged reactants) with a common solvation sphere (eq 1). The electron transfer takes place within this complex to form a successor complex (eq 2), which dissociates to the observed reaction products (eq 3). A composite rate law (eq 4) can be derived for eq 1–3 if the precursor complex formation

$$\text{rate} = \frac{k_{et}K_0[\text{M(III)}][\text{N(II)}]}{1 + K_0[\text{M(III)}]} \qquad K_0 = \frac{k_1}{k_{-1}} \tag{4}$$

is a rapidly established preequilibrium and the electron transfer is rate determining ($k_{-1} >> k_{et}$). For many systems with like-charged reactants eq 4 reduces to a second-order rate law (eq 5). In a number of instances[2-6] it has been possible to

$$\text{rate} = k[\text{M(III)}][\text{N(II)}] \qquad k = k_{et}K_0 \tag{5}$$

measure the intramolecular rate constant, k_{et}, for the electron transfer within an ion pair. Oliveira, Giesbrecht, and Toma[6] have shown that a linear correlation exists between ln k_{et} values for the reductions of $[(NH_3)_5Co(Me_2SO)]^{3+}$ by a series of $[Fe(CN)_5L]^{3-}$ reductants and their respective reduction potentials. The analogous experiment demonstrating the effect of the half-wave potentials of complexes of cobalt(III) (within an ion pair with a common reductant) on the intramolecular electron-transfer rate constant has not been performed to date mainly because the potentials of the Co^{3+}/Co^{2+} couple for normal Werner-type complexes are not known.

Binuclear μ-carboxylato complexes of cobalt(III) should represent a useful class of compounds to study the effect of an increasing electron-withdrawing capacity of the substituent, R, on the rate of outer-sphere electron-transfer with various reducing agents. The aim of the present study was to unambiguously assess an electronic inductive effect of a remote substituent on the rate of electron-transfer reactions. For the inner-sphere reductions of (carboxylato)pentaamminecobalt(III) complexes by $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Eu(OH_2)_6]^{2+}$ the inductive effect has always been obscured by steric effects of the substituents on the inner-sphere-type precursor formation constants:[7-9] the (acetato)pentaamminecobalt(III) complex is faster reduced by Cr(II) than its trifluoroacetate analogue, and the formato complex is more rapidly reduced than either of these. In fact, linear correlations between log k_{redn} and Taft's *steric* substituent parameters (E_s) have been found.[8,9] In addition, binuclear μ-carboxylato complexes of cobalt(III) with large hydrophobic substituents [R = naphthalene (I), quinoline (II), pyridine (III)] were reduced with $[Fe(dipic)_2]^{2-}$ in order to increase the ion-pair formation constant, K_0, and measure the intramolecular electron-transfer rate constant, k_{et}, in eq 4.

Experimental Section

(a) Preparation of Reagents and Solutions. The preparation and characterization of most of the μ-(carboxylato)-dicobalt(III) complexes have been described by Siebert and Tremmel.[10] The perchlorate salts of μ-formato, μ-acetato, μ-(fluoroacetato), μ-(difluoroacetato), and μ-(trifluoroacetato) were prepared accordingly. From preliminary

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[1] Sutin, N. "Bioinorganic Chemistry"; Eichhorn, G. L., Ed.; American Elsevier: New York, 1973; Vol. 2.

[2] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883.

[3] Gaswick, D.; Haim, A. *J. Am. Chem. Soc.* **1971**, *93*, 7347.

[4] Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.

[5] Oliveira, L. A. A.; Toma, H. E.; Giesbrecht, E. *Inorg. Chim. Acta* **1977**, *22*, 269.

[6] Oliveira, L. A. A.; Giesbrecht, E.; Toma, H. E. *J. Chem. Soc., Dalton Trans.* **1979**, 236.

[7] Barrett, M. B.; Swinehart, J. H.; Taube, H. *Inorg. Chem.* **1971**, *10*, 1983.

[8] (a) Chen, J. C.; Gould, E. S. *J. Am. Chem. Soc.* **1973**, *95*, 5539. (b) Gould, E. S.; Taube, H. *Ibid.* **1964**, *86*, 1318. (c) Gould, E. S. *Ibid.* **1965**, *87*, 4370; **1966**, *88*, 2983; **1967**, *89*, 5792.

[9] Fan, F. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2639.

[10] Siebert, H.; Tremmel, G. *Z. Anorg. Allg. Chem.* **1972**, *390*, 292.

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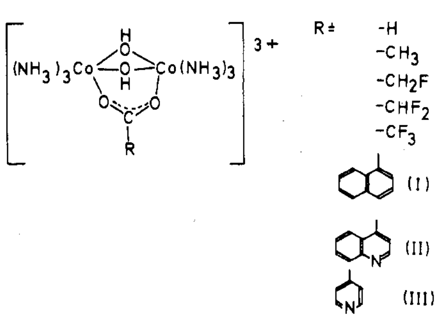

kinetic experiments it was found that these complexes were contaminated with a relatively more reactive species (1–2%). Therefore, recrystallization of complexes from aqueous solutions with concentrated $HClO_4$ at 2 °C was repeated until the observed pseudo-first-order rate constant (excess oxidant) for a standardized reduction by $[Fe(dipic)_2]^{2-}$ reached a limiting value which was in all cases smaller than the first measured value. Finally, the individual run followed strictly first-order kinetics for at least 4 half-lives of the reaction. It was found that three recrystallizations gave satisfactorily pure samples. Since concentrated $HClO_4$ was used, only the triperchlorate salts were obtained (in the original paper[10] $NaClO_4$ was used and double salts containing $NaClO_4$ are reported), which were dried over P_2O_5 at 40 °C for 1 week after which time the samples did not contain any water of crystallization.

The μ-(pyridine-4-carboxylato)-dicobalt(III) complex was prepared as described elsewhere.[11] The μ-(naphthalene-1-carboxylato)- and the μ-(quinoline-4-carboxylato)-dicobalt(III) complexes were pepared for the first time according to the literature procedure.[11] The elemental analyses (Co, N, C, H) of dried samples gave satisfactory values for the triperchlorate salt (μ-naphthalene complex) or for the tetraperchlorate salts of complexes with N-heterocyclic ligands.

For kinetic experiments with $[Ru(NH_3)_6]^{2+}$ the bromide salts of the μ-(carboxylato)-dicobalt(III) complexes[10] were used since ClO_4^- oxidizes $[Ru(NH_3)_6]^{2+}$.

Stock solutions of $[Fe(OH_2)_6]^{2+}$ in perchloric acid were prepared by dissolving iron metal in 1 M $HClO_4$ under an argon atmosphere. Solutions containing the $[Ti(OH_2)_6]^{3+}$ ion were prepared by dissolving titanium hydride in 1 M HCl at 50 °C (~60 h). Solutions of $[V(OH_2)_6]^{2+}$ and $[Cr(OH_2)_6]^{2+}$ in perchloric acid were prepared by electrolytic reductions of solutions of vanadium(IV) perchlorate and hexaaquochromium(III) perchlorate, respectively. Solutions of $[Ru(NH_3)_6]^{2+}$ were prepared by reducing recrystallized $[Ru(NH_3)_6]Cl_3$ over a zinc amalgam. These solutions were used within 2 h of their peparation. Deionized water was distilled and then used for kinetic experiments.

(b) Instrumentation and Kinetic Measurements. Standard syringe techniques were used for all electron-transfer reactions with use of argon as blanketing gas throughout this study. All kinetic measurements were made on a UNICAM SP 1700 spectrophotometer interfaced to a Commodore PET 2001 computer for data acquisition and analysis. All reactions were run under pseudo-first-order conditions with the dicobalt(III) complexes in excess over the reductants $[Fe(dipic)_2]^{2-}$ and $[Ti(dipic)_2]^-$, respectively, both of which were generated in situ from $[Fe(OH_2)_6]^{3+}$ or $[Ti(OH_2)_6]^{3+}$ and dipicolinic acid as described previously.[12] Reductions with $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Ru(NH_3)_6]^{2+}$ were carried out with the respective reductant being the excess component. Pseudo-first-order rate constants were calculated by using a least-squares program[13] where the absorptions at the beginning ($t = 0$) and after the completed reaction ($t = \infty$) were treated as variables. The observed and calculated values differed only within the uncertainty of the last digit of the readings of the instrument. The reproducibility of replicate runs was better than 3% for all reductants except for $[Ru(NH_3)_6]^{2+}$ (8%).

Results

(a) Reductions of μ-(Carboxylato)-dicobalt(III) Complexes with $[Fe(dipic)_2]^{2-}$. The stoichiometry of the reductions of binuclear complexes of cobalt(III), $[Co^{III}_2]^{3+}$, by $[Fe(dipic)_2]^{2-}$ is as in eq 6. Reduction of the first Co(III) is the rate-determining step in all cases. The kinetics of the reductions were studied at pH 5.0 in an acetate buffer (0.066 M) by using pseudo-first-order conditions with $[Co^{III}_2]$ in excess over $[Fe(dipic)_2]^{2-}$ and an ionic strength of 0.16 M ($LiClO_4$). The decrease in absorbance at λ = 485 nm was followed as a function of time. The observed pseudo-first-order rate constants for the reductions of μ-(naphthalene-1-carboxylato)- and the μ-(quinoline-4-carboxylato)-dicobalt(III) complexes showed a dependence on $[dipic^{2-}]$ (at pH 5.0 the actual concentration of the $dipic^{2-}$ dianion corresponds to the total concentration of dipicolinic acid used) and on $[Co^{III}_2]_t$, the total concentration of the $[Co^{III}_2]^{3+}$ complexes. The functional dependence conforms to eq 7.

$$[Co^{III}_2]^{3+} + 2[Fe(dipic)_2]^{2-} \rightarrow 2Co^{II} + 2[Fe(dipic)_2]^- \quad (6)$$

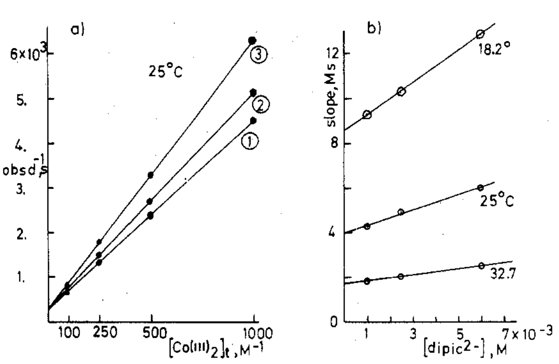

Figure 1. Graphical evaluation of ion-pair association constants (K, K_0) and of the intramolecular rate constants (k_{et}, eq 7) for the reduction of the μ-(naphthalene-1-carboxylato)-dicobalt(III) cation by $[Fe(dipic)_2]^{2-}$: (a) plot of k_{obsd}^{-1} (s) vs. $[Co^{III}_2]_t^{-1}$ (M^{-1}) at 25 °C and various concentrations of $[dipic^{2-}]$ (① = 1×10^{-3} M, ② = 2.5×10^{-3} M, ③ = 6.0×10^{-3} M); (b) plot of the slopes of straight lines from Figure 1a vs. $[dipic^{2-}]$ at different temperatures (18.2, 25.0, 32.7 °C).

$$k_{obsd} = \frac{k_{et}K_0[Co^{III}_2]_t}{1 + K_0[Co^{III}_2]_t + K[dipic^{2-}]} \quad (7)$$

A mechanism as is depicted in eq 8a–c leads to rate law 8d,

$$[Co^{III}_2]^{3+} + [Fe(dipic)_2]^{2-} \rightleftharpoons \{[Co^{III}_2]^{3+}[Fe(dipic)_2]^{2-}\}^+ \quad K_0 \quad (8a)$$

$$[Co^{III}_2]^{3+} + dipic^{2-} \rightleftharpoons \{[Co^{III}_2]^{3+}dipic^{2-}\}^+ \quad K \quad (8b)$$

$$\{[Co^{III}_2]^{3+}[Fe(dipic)_2]^{2-}\}^+ \xrightarrow{k_{et}} \text{products} \quad (8c)$$

$$k_{obsd} = \frac{k_{et}K_0[Co^{III}_2]_t}{1 + K_0[Co^{III}_2]_t + K[dipic^{2-}] + K_0[Fe(dipic)_2]} \quad (8d)$$

where K_0 is the formation constant of the redox-active outer-sphere precursor complex (ion pair), k_{et} is the intramolecular electron-transfer rate constant, and K is the equilibrium constant for ion pairing between the uncomplexed dianion, $dipic^{2-}$, and the cobalt(III) complex. Due to the reduced overall charge of the latter ion pair (1+) further association of this species with $[Fe(dipic)_2]^{2-}$ yielding a second redox-active precursor complex is not considered to contribute significantly to the overall rate of reduction. Under our experimental conditions $K_0[Fe(dipic)_2] \leq K_0[Co^{III}_2]_t \simeq K[dipic^{2-}] << 1$ because $[Fe(II)] = 10^{-4}$ M, $K_0 \approx K \approx 60$ M^{-1}, $[Co^{III}_2] > 10^{-3}$ M, and $[dipic^{2-}] > 10^{-3}$ M. Therefore, rearrangement of eq 8 gives eq 9 which is the reciprocal of eq 7, and plots of k_{obsd}^{-1}

$$k_{obsd}^{-1} = \frac{1 + K[dipic^{2-}]}{k_{et}K_0[Co^{III}_2]_t} + \frac{1}{k_{et}} \quad (9)$$

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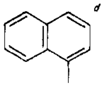
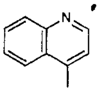
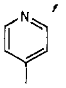
[11] Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1973**, 2538.
[12] Bertram, H.; Wieghardt, K. *Inorg. Chem.* **1979**, *18*, 1799.
[13] DeTar, D. F. *Comput. Chem.* **1978**, *2*, 99.
[14] Second-order rate constants, k_{Ru} (M^{-1} s^{-1}), for these reductions were taken from: Fan, F. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

Table I. Intramolecular Rate Constants for the Reductions of μ-(Carboxylato)-dicobalt(III) Complexes with $[Fe(dipic)_2]^{2-}$ [a]

R	T, °C	10^3k_{et}, s^{-1}	K_0, M^{-1}	K, M^{-1}
 [d]	18.2	1.87	63	84
	25.0	3.94	64	84
	32.8	11.45	51	69
	43.2	30.4		
 [e]	15.2	2.52	63	102
	25.0	7.73	54	62
	33.9	23.4		
	41.5	42.1	58	64
 [f]	25	1.61 [b]	50 [c]	66
	33.1	4.1	50	40
	43.6	14.2	50	72

[a] $[[Fe(dipic)_2]^{2-}] = 1 \times 10^{-4}$ M, pH 5.0 (acetate buffer), $I =$ 0.16 M ($LiClO_4$), $[dipic^{2-}] = (1–6) \times 10^{-3}$ M. [b] Calculated from $k_{et}K_0 = k_{Fe}$ (25 °C, 0.08; 33.1 °C, 0.20; 43.6 °C, 0.71) with $K_0 = 50$ M^{-1}. [c] Estimated on the basis $K/K_0 = 1.31$ and an average value of 66 M^{-1} for K. [d] $\Delta H^{\ddagger} = 20.2 \pm 1$ kcal/mol; $\Delta S^{\ddagger} = -1.6 \pm 3$ cal K^{-1} mol^{-1}. [e] $\Delta H^{\ddagger} = 19.1 \pm 0.9$ kcal/mol; $\Delta S^{\ddagger} = -4 \pm 3$ cal K^{-1} mol^{-1}. [f] $\Delta H^{\ddagger} = 21.4 \pm 1.5$ kcal/mol; $\Delta S^{\ddagger} = 0.3 \pm 5$ cal K^{-1} mol^{-1}.

vs. $[Co^{III}{}_2]_t^{-1}$ with $[dipic^{2-}]$ = constant should give straight lines with a common intercept ($=k_{et}^{-1}$, s) and a slope ($=(1 + K[dipic^{2-}])/k_{et}K_0$). This is shown in Figure 1a. Plots of these respective slopes vs. $[dipic^{2-}]$ should again afford straight lines with an intercept ($=(k_{et}K_0)^{-1}$) and a slope ($=K/k_{et}K_0$). This is shown in Figure 1b for different temperatures. Thus it has been possible to evaluate graphically the intramolecular rate constants and the ion-pair association constants, K_0 and K, at various temperatures for the μ-(naphthalene-1-carboxylato) and the μ-(quinoline-4-carboxylato) complexes. The results are summarized in Table I.

In contrast, plots of k_{obsd}^{-1} vs. $[Co^{III}{}_2]_t^{-1}$ for the reductions of all other complexes of the present study by $[Fe(dipic)_2]^{2-}$ yield straight lines passing through the origin (see, for example, Figure 2a), the slopes of which depend on the respective $[dipic^{2-}]$ concentration. No intercepts ($=k_{et}^{-1}$) can be determined experimentally since $1/k_{et}$ is relatively too small to be detected; eq 9 simplifies to eq 10. From plots of the slopes

$$k_{obsd}^{-1} = \frac{1 + K[dipic^{2-}]}{k_{et}K_0[Co^{III}{}_2]_t} \tag{10}$$

of these straight lines vs. $[dipic^{2-}]$ second-order constants, $k = k_{et}K_0$, and, in addition, the association constant, K (Figure 2b), were evaluated.

Numerical values of K for the ion pairing of $dipic^{2-}$ and substituted μ-(acetato)-dicobalt(III) complexes do not vary much (Table II; $K \approx 35$ M^{-1} at 25 °C), but they are significantly smaller than those observed for complexes where stacking of aromatic rings in combination with hydrophobic interactions between the oxidants and $dipic^{2-}$ is possible (Table I; $K \approx 60$ M^{-1} at 25 °C).

Contrary to an earlier report[12] we have not been able to determine k_{et} for the μ-(pyridine-4-carboxylato)-dicobalt(III) complex. The previously observed intercept in the plot of k_{obsd}^{-1} vs. $[Co^{III}{}_2]_t^{-1}$ is an artifact due to an insufficient purity of the binuclear complex used.

From the now measured dependence of the rates of reductions on $[dipic^{2-}]$ and the subsequent evaluation of association constants, K, it is possible to estimate the magnitudes of the intramolecular electron-transfer rate constants. The measured K is used as an auxiliary variable to get a reasonable estimate of K_0 if one assumes that the *ratio* $K/K_0 \simeq 1.3$ is approximately *independent* of the structural details of the respective dicobalt(III) complex involved in the ion pairing. The ratio $K/K_0 \simeq 1.3$ has been determined for the μ-(naphthalene-1-carboxylato) and μ-(quinoline-4-carboxylato) complexes, respectively (Table I).

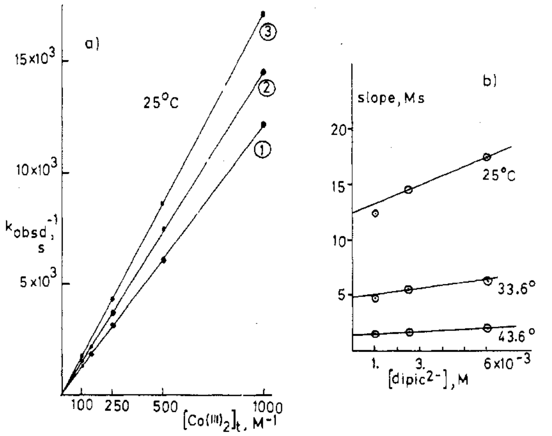


Figure 2. Graphical evaluation of the ion-pair association constant, K, and the second-order rate constant [$k_{Fe} = k_{et}K_0$ (M^{-1} s^{-1})] for the reduction of the μ-(pyridine-4-carboxylato)-dicobalt(III) cation by $[Fe(dipic)_2]^{2-}$: (a) plot of k_{obsd}^{-1} vs. $[Co^{III}{}_2]_t^{-1}$ at 25 °C and various concentrations of $[dipic^{2-}]$ (① = 1×10^{-3} M, ② = 2.5×10^{-3} M, ③ = 6.0×10^{-3} M; (b) plot of slopes of straight lines from Figure 2a vs. $[dipic^{2-}]$ at different temperatures (25, 33.6, 43.6 °C).

Table II. Summary of Kinetic Data for the Reductions of μ-(Carboxylato)-dicobalt(III) Cations by $[Fe(dipic)_2]^{2-}$ at 25 °C, pH 5.0 (Acetate Buffer 0.07), and $I = 0.16$ ($LiClO_4$)

R	$10^2k_{et}K_0$, M^{-1} s^{-1}	K, M^{-1}	10^3k_{et}(calcd),[a] s^{-1}
CH_3	1.43	43	0.436
CH_2F	5.08	34	1.96
CHF_2	11.9	33	4.7
CF_3	28.6	31	12.1
H	4.1	69	0.78

[a] Calculated on the assumption that $K_0 = 0.76K$.

The important result of this type of calculation is that the ion-pair association constants, K_0, for the formation of the redox-active precursor complexes are very similar for the series of substituted μ-(acetato)-dicobalt(III) complexes (Table II). The variation of the rates of reductions *cannot* be ascribed to differences in the precursor complex formation constants. These calculated intramolecular rate constants vary from 0.44 × 10^{-3} s^{-1} for the μ-acetato complex to 12.1 × 10^{-3} s^{-1} for its μ-(trifluoroacetato) analogue.

Figure 3 demonstrates that a linear correlation exists between the logarithm of the intramolecular electron-transfer rate constant, log k_{et} (or, alternatively, log ($k_{et}K_0/K$) which represents a *measured* quantity), and Taft's inductive parameters,[21] σ_I (or the pK_a values of the acid dissociation constants of the uncomplexed organic acid), for the series of structurally very similar μ-(acetato)-dicobalt(III) complexes. Interestingly, the μ-formato complex fits the same correlation.

On the other hand, the presence of large hydrophobic substituents at the μ-carboxylato bridge leads to structurally different redox-active precursor complexes since they do not fit the correlation. In the case of the μ-(naphthalene-1-carboxylato) and the μ-(quinoline-4-carboxylato) complexes the intramolecular electron transfer is most probably facilitated by stacking of the aromatic rings, and transport of the electron occurs through the π systems. It must be emphasized that the redox-active metal ions Co(III) and Fe(II) in such stacked structures are further apart (~1 Å) from each other than is also conceivable if ion-pairing occurs at the OH bridges or NH_3 ligands of the oxidants. In the latter instance there would be no two distinct structures for the redox-active ion pairs. It is noted that the intramolecular rate constants for electron transfer in the stacked systems appear to be also a function

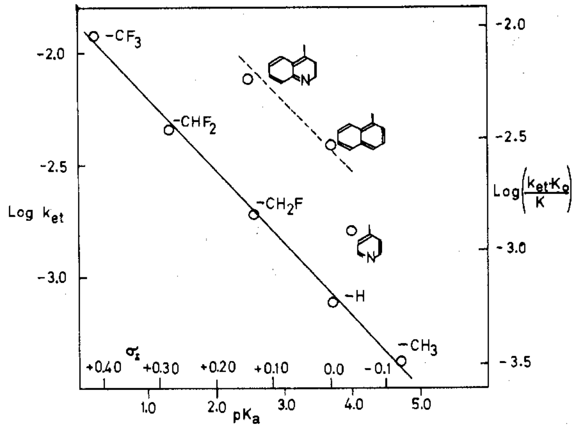
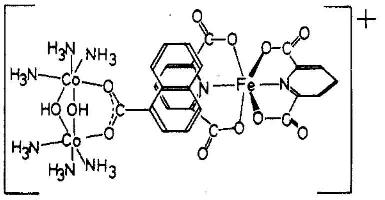


Figure 3. Correlations of measured values of log $(k_{et}K_0/K)$ (or, alternatively, calculated values of log k_{et}) vs. the pK_a values of acid dissociation constants of uncomplexed organic acids (or, alternatively, inductive constants, σ_I) for the reductions of a series of μ-(carboxylato)-dicobalt(III) complexes by $[Fe(dipic)_2]^{2-}$. The broken line connects measured log k_{et} values [or *measured* log $(k_{et}K_0/K)$ values] for the respective reductions of μ-(naphthalene-1-carboxylato)- and μ-(quinoline-4-carboxylato)-dicobalt(III) complexes (see text).

of Taft's inductive parameter, σ_I (broken line in Figure 3). The reactivity difference of these complexes is reflected in differences of the enthalpy of activation (Table I)—although the effect is admittedly very small and may not be significant.



(b) Reductions of μ-(Carboxylato)-dicobalt(III) Complexes with $[Ti(dipic)_2]^-$. The stoichiometry of the reductions of binuclear complexes of cobalt(III) by $Ti(dipic)_2^-$ is as in eq 11. Reduction of the first Co(III) center is the rate-determining step in all cases. $[Ti(dipic)_2]^-$ was prepared in situ from solutions of $[Ti(OH_2)_6]^{3+}$ and dipic^{2-} as described previously.[12] The kinetics of the reductions were studied at pH 5.0 (acetate buffer, 0.066 M), an ionic strength of 0.16 M ($LiClO_4$), and 25 °C by using pseudo-first-order conditions with $[Co^{III}_2]_t$ in large excess over [Ti(III)] (1×10^{-4} M). The decrease in absorbance was followed at $\lambda = 513$ nm as a function of time. Variation of k_{obsd} on [dipic^{2-}] and on $[Co^{III}_2]_t$ conformed to eq 10. Therefore, it has not been possible to determine k_{et} from kinetic measurements. Since the effect of [dipic^{2-}] on k_{obsd} was found to be relatively small over a range [dipic^{2-}] = $(1.0–6.0) \times 10^{-3}$ M, it was decided to investigate the kinetics at a constant concentration of [dipic^{2-}] (2.5×10^{-3} M):

$$[Co^{III}_2]^{3+} + 2[Ti(dipic)_2]^- \rightarrow 2Co^{II} + 2[Ti(dipic)_2]^0 \qquad (11)$$

$$k_{obsd} = k'_{Ti}[Co^{III}_2]_t$$

where

$$k'_{Ti} = (1 + K(2.5 \times 10^{-3}))^{-1}k_{et}K_0 \qquad (12)$$

For the series of μ-(acetato)-dicobalt(III) complexes $K \approx 33$ M^{-1} at 25 °C (Table II). Consequently, we estimate the true second-order rate constants, $k_{Ti} = k_{et}K_0$, for the reductions by $[Ti(dipic)_2]^-$ to be larger by ca. 8% than the measured values of k'_{Ti} (Table III). Figure 4 shows that an excellent linear correlation exists between log k'_{Ti} and the pK_a of the uncomplexed organic acid. The latter may be substituted by Taft's inductive parameters, σ_I.

Table III. Summary of Kinetic Data [$k_{redn} = k_{et}K_0$ (M^{-1} s^{-1})] for the Reductions of μ-(Carboxylato)-dicobalt(III) Cations by $[Ti(dipic)_2]^-$, $[Ru(NH_3)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Cr(OH_2)_6]^{2+}$

R	k'_{Ti}[a]	k_{Ru}[b]	k_V[c]	$10^3 k_{Cr}$[c]
CH_3	0.59	0.035	0.062	1.46
CH_2F	1.97	0.12	0.13	2.79
CHF_2	3.83	0.21	0.21	3.97
CF_3	8.02	0.36	0.38	6.30
H	1.18		0.113	2.72

[a] pH 5 (acetate buffer 0.07 M), $I = 0.16$ M (LiCl), [Ti(III)] = (1 + K[dipic]). Since K[dipic] = 0.088 the true second-order rate constants, $k_{et}K_0$, are estimated to be 8% larger. [b] $[H^+] = 0.1$ M, $[Co^{III}_2] = 1 \times 10^{-3}$ M, $I = 0.15$ M (LiCl). [c] $[H^+] = 0.1$ M, $[Co^{III}_2] = 1 \times 10^{-3}$ M, $I = 1.0$ M ($LiClO_4$).

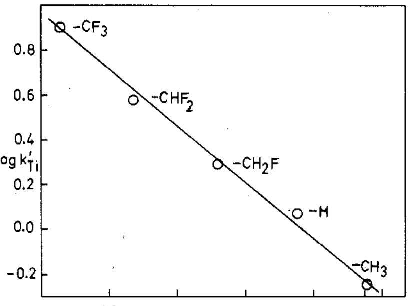


Figure 4. Correlation of log k'_{Ti} values vs. pK_a values of uncomplexed organic acids [$k'_{Ti} = k_{et}K_0/(1 + K[\text{dipic}])$ with [dipic] = 2.5×10^{-3} M] for the reductions of μ-(acetato)-dicobalt(III) complexes by $[Ti(dipic)_2]^-$ at 25 °C.

(c) Reductions of μ-(Carboxylato)-dicobalt(III) Complexes with $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Ru(NH_3)_6]^{2+}$. The stoichiometry of the reductions of binuclear complexes of cobalt(III) by $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Ru(NH_3)_6]^{2+}$, respectively, is as in eq 13, where redn^{2+} = $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Ru(NH_3)_6]^{2+}$. Reduction of the first Co(III) center is the rate-determining step. The kinetics of the reductions were studied at 25 °C, $[H^+] = 0.1$ M, and $I = 1.0$ M ($LiClO_4$ was the supporting electrolyte for the reductions by Cr(II) and V(II) whereas LiCl was used for $[Ru(NH_3)_6]^{2+}$ reductions, $I = 0.15$ M) by using pseudo-first-order conditions with the respective reductant in large excess. Observed pseudo-first-order rate constants (see supplementary material) conform to eq 14. Numerical values for the second-order rate constants are listed in Table III.

$$[Co^{III}_2]^{3+} + 2\text{redn}^{2+} \rightarrow 2Co^{II} + 2\text{redn}^{3+} \qquad (13)$$

$$k_{obsd} = k_{redn}[\text{redn}] \qquad (14)$$

In Figures 4–6 it is shown that again linear correlations exist between log k_{redn} and the pK_a values of the uncomplexed organic acids (or σ_I values). It is of interest that, when the outer-sphere reductant $Ru(NH_3)_6^{2+}$ reduces three mononuclear complexes $[(NH_3)_5Co(O_2CR)]^{2+}$ (R = CF_3, CHF_2, CH_3),[14] a linear correlation between log k_{Ru} and the pK_a values of uncomplexed acids is also found. The slopes of the two correlations in Figure 5 are identical within experimental error.

Note that the order of reactivity (log k_{redn} = log $k_{et}K_0$) for the reductions of the series of μ-(acetato)-dicobalt(III) complexes by a common reductant does *not* change when the charge of the reductant y changes from 2– or 1– {$[Fe(dipic)_2]^{2-}$, $[Ti(dipic)_2]^-$} to 2+ {$[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Ru(NH_3)_6]^{2+}$}: in all cases $k_{CF_3,y} > k_{CHF_2,y} > k_{CH_2F,y} > k_{CH_3,y}$. Thus the differences of reactivities cannot be accounted for by simple variation of the outer-sphere association constants,

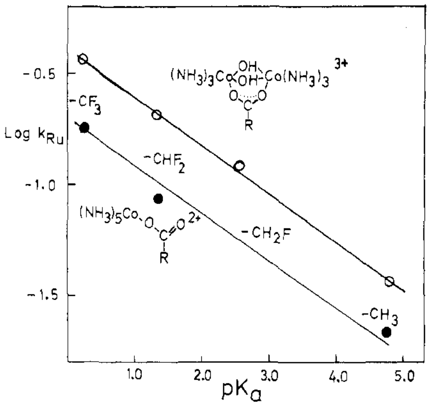


Figure 5. Correlations of log k_{Ru} values vs. pK_a of uncomplexed organic acids for the outer-sphere reductions of binuclear (○) μ-(acetato)-dicobalt(II) complexes and of mononuclear (●) pentaammine(carboxylato)cobalt(III) complexes by $[Ru(NH_3)_6]^{2+}$, respectively.

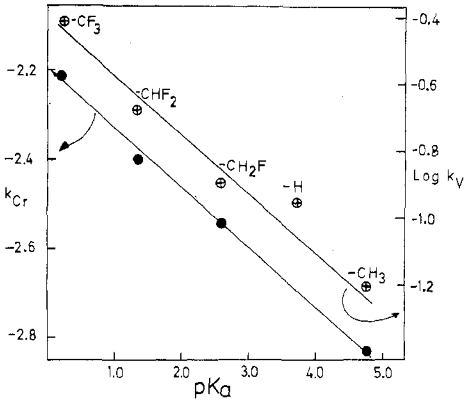


Figure 6. Correlations of log k_{Cr} (●) and of log k_V (○) vs. pK_a values of uncomplexed organic acids for the outer-sphere reductions of μ-(acetato)-dicobalt(III) complexes by $[Cr(OH_2)_6]^{2+}$ and $[V(OH_2)_6]^{2+}$ at 25 °C, respectively.

K_0, within the series of oxidants in which case an inversion of the reactivity pattern would be expected. Although the "instability" constants for the encounter complex formation between the reductants $Cr(OH_2)_6^{2+}$, $V(OH_2)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ and the dicobalt(III) oxidants are not known, it is reasonable to suggest (on the basis of the results obtained for the reductions with $Fe(dipic)_2^{2-}$) that they are constant—at least for the series of μ-acetato complexes.

Discussion

(a) Assessment of an Inductive Effect on the Rates of Electron-Transfer Reactions. It has long been recognized that the predominant factor determining relative rates of reduction, $k_{x,y}$, of most common cobalt(III) complexes x by outer-sphere reductants y is the variation in free energy of the reaction, $\Delta G°_{x,y}$. Endicott et al.[15] have demonstrated a linear relationship (eq 15) for the reduction of a series of macrocyclic

$$-2.3RT \log k_{x,y} = a + b\Delta G°_{x,y} \qquad (15)$$

cobalt(III) complexes by $Ru(NH_3)_6^{2+}$ and $V(OH_2)_6^{2+}$, respectively, where a is a constant for a given reductant y (and only weakly dependent on the nature of the cobalt oxidant) whereas b was found to be independent of the nature of the reductant y and of the oxidant x.[16] Eq 15 may be rearranged to give eq 16 where E_0^x and E_0^y are the normal potentials of

$$\log k_{x,y} = \frac{b}{0.059}(E_0^x - E_0^y) + \text{constant} \qquad (16)$$

the oxidant x and the reductant y, respectively. Eq 16 is derived for one-electron-transfer reactions at 25 °C.

Oliveira et al.[6] have shown that the rate of intramolecular electron transfer within an ion pair $\{[Co(NH_3)_5(Me_2SO)]^{3+}[Fe(CN)_5L]^{3-}\}$ is a linear function of the half-wave potentials of the reductants, $[Fe(CN)_5L]^{3-}$, with the predicted[16] slope for b in eq 16 of 0.5. The analogous experiments varying the oxidation potentials of cobalt(III) complexes are frustrated by the fact that it is not possible to measure the E_0^x potentials for the Co^{3+}/Co^{2+} couple of simple Werner-type complexes.

For the present series of μ-(carboxylato)-dicobalt(III) complexes it has been shown that a linear relationship exists between the basicity of the oxygen atoms of the uncomplexed organic acid (this is expressed in terms of their respective pK_a value) and the antisymmetric (C–O) stretching frequencies, ν(C–O), of the symmetrically bonded[17] carboxylato groups in the dicobalt(III) complexes. Furthermore, ^{59}Co NMR spectroscopy of these complexes revealed that the ^{59}Co relaxation is a linear function of the basicity of the O atoms of the carboxylato bridging groups affecting the electric field gradient at the Co nuclei.[18] Thus an electronic effect is transmitted from the remote substituents on the carboxylate groups onto the Co(III) centers. Recently, linear relationships between the half-wave potentials for the couples Fe^{3+}/Fe^{2+} [19] or Ni^{3+}/Ni^{2+} [20] of macrocyclic complexes and the inductive parameter, σ_I, of substituents on the respective macrocyclic ligands have been demonstrated (eq 17). Therefore, we feel

$$E_0 = \text{constant} + d(\sigma_I) \qquad (17)$$

it is reasonable to assume that E_0^x values of the Co^{3+}/Co^{2+} couple for the series of μ-carboxylato complexes are also linearly correlated with Taft's inductive parameter,[21] σ_I, of substituents such as CH_3, CH_2F, CHF_2, and CF_3 according to eq 17.

The CF_3 group exerts the most prominent electron-withdrawing effect which increases the oxidizing capability of the two Co(III) centers whereas the CH_3 group reduces somewhat the positive charge at the Co(III) nuclei and decreases the oxidizing power of the Co(III) ions. The observed order of reactivity [$\log k_{x,y} = \log k_{et}^{x,y}K_0$ (x = oxidant, y = reductant] for the reductions of the series of μ-(acetato)-dicobalt(III) complexes by a reductant y {y = $[Fe(dipic)_2]^{2-}$, $[Ti(dipic)_2]^-$, $[Ru(NH_3)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Cr(OH_2)_6]^{2+}$} is the same in all cases: $k_{CF_3} > k_{CHF_2,y} > k_{CH_2F,y} > k_{CH_3,y}$ (Table II and III, Figures 3–5). This is taken as evidence for the validity of eq 15 and 16. As the oxidizing ability of cobalt(III) is increased, $\Delta G°_{x,y}$ of the reaction is increased by using different complexes of cobalt(III), but the same reductant y and, consequently, log $k_{x,y}$ increases.

To summarize, we have shown for a series of structurally very similar oxidants x of cobalt(III) which are reduced by a common reductant y that linear relationships exist between log $k_{x,y}$ and the inductive parameter of remote substituents of the oxidants.

(b) Assessment of Selectivity in Outer-Sphere Electron-Transfer Reactions. A unique feature of the outer-sphere reductions of the present series of μ-(acetato)-dicobalt(III) complexes by a common reductant y is the remarkable

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(15) Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 394.

(16) The Marcus cross relation for outer-sphere reductions in its simplest form, $k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$, predicts b (eq 15) to be 0.5. This has been verified experimentally in a few cases.[6,15]

(17) Maas, G. *Z. Anorg. Allg. Chem.* **1977**, *432*, 203.

(18) Hackbusch, W.; Rupp, H. H.; Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1975**, 2364.

(19) Goel, R. G.; Henry, P. M.; Polyzou, P. C. *Inorg. Chem.* **1979**, *18*, 2148.

(20) Pillsbury, D. G.; Busch, D. H. *J. Am. Chem. Soc.* **1976**, *98*, 7836.

(21) Values for Taft's inductive parameters, σ_I, were taken from: "Correlation Analysis in Chemistry"; Plenum Press: New York and London, 1978; Chapter 10.

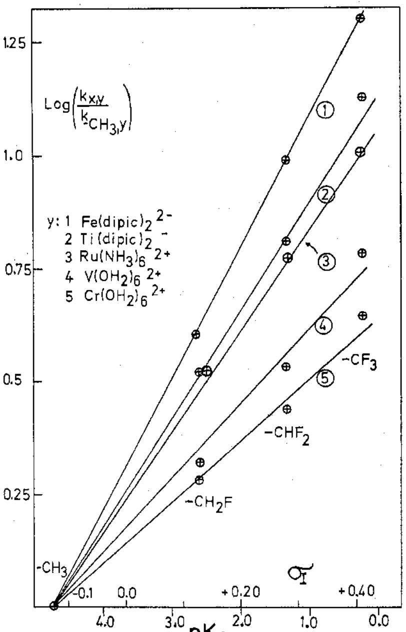

Figure 7. Correlation of the selectivity of reductions of dicobalt(III) complexes [i.e., the reactivity, log $k_{x,y}$, of the reduction of a substituted μ-(acetato)-dicobalt complex x by a reductant y minus the reactivity, log $k_{CH_3,y}$, of the reduction of the μ-(acetato)-di-μ-hydroxo-bis[triamminecobalt(III)] complex] by the same reductant y vs. the inductive parameter σ_I of the substituents, R, of the binuclear oxidants.

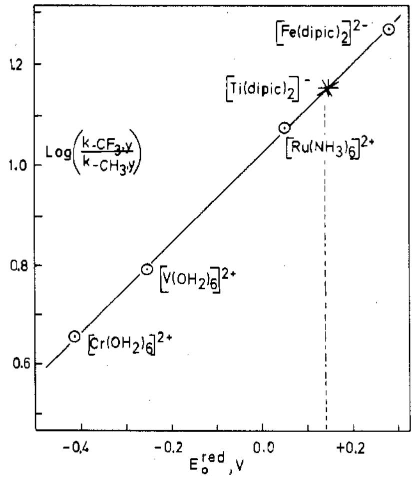

Figure 8. Correlation of the selectivity (log $k_{CF_3,y}$ − log $k_{CH_3,y}$) of the reductions of the μ-(trifluoroacetato)- and μ-(acetato)-dicobalt(III) complexes by a common reductant y vs. the normal reduction potentials, E_0^{redn}, of the respective reductant y. The value of E_0 for the couple $[Ti(dipic)_2]^-/[Ti(dipic)_2]^0$ is not known; from the measured selectivity this value is estimated to be +0.13 V (broken line).

structural similarity of the redox-active precursor complexes which are ion pairs (opposite charges of reactants) or encounter complexes (like-charged species). Since the charge (3+) and the steric conditions of the oxidants with R = CH_3, CH_2F, CHF_2, and CF_3 are nearly identical, the outer-sphere association constants, K_0, for the formation of precursor complexes between these oxidants and a common reductant have almost the same numerical values. This has been established experimentally to be most probably true for the reductant $[Fe(dipic)_2]^{2-}$ (Table II).

It is therefore meaningful to compare differences of reactivities within a series of reductions by a reductant y, e.g., log $k_{CF_3,y}$ − log $k_{CH_3,y}$, because the values for K_0 for a given reductant y cancel each other: $k_{CF_3,y} = k_{et}^{CF_3,y}K_0$; $k_{CH_3,y} = k_{et}^{CH_3,y}K_0$. In this way we are dealing with relative reactivities (or selectivities) within the redox-active ion pairs or encounter complexes. The individual work terms of bringing the reactants together in solution no longer have to be considered.[37]

The effect of the increasing oxidizing power of the Co(III) centers on these relative intramolecular electron-transfer rates is shown in Figure 7. Plots of log $k_{x,y}$ − log $k_{CH_3,y}$ vs. σ_I give nice linear correlations for each reductant y. This is of course only a restatement of eq 16 (see eq 18). It is assumed that

$$\log k_{x,y} - \log k_{CH_3,y} = \frac{b_y}{0.059}(E_0^{x} - E_0^{CH_3}) \qquad (18)$$

the constant in eq 16 will not be dependent on the nature of the cobalt(III) oxidant. Substituting E_0^x values in eq 18 for the appropriate values for σ_I with use of eq 17 one obtains eq 19.

$$\log k_{x,y} - \log k_{CH_3,y} = \frac{b_y d}{0.059}(\sigma_I^{x} - \sigma_I^{CH_3}) \qquad (19)$$

The most interesting result of this study is the observation that the slopes of the straight lines in Figure 7 are different for each reductant y. Contrary to Endicott's results[15] the proportionality factor b in eq 15 is *not* constant for various reductants but is a function of some property or other of the reducing agent. This result is also in conflict with the simple Marcus cross relation.[16,37] In other words, the selectivity,[22] i.e., the difference of reactivities within the precursor complexes (log $k_{et}^{CF_3,y}$ − log $k_{et}^{CH_3,y}$), is a function of the respective reductant y. For two different reductants y1 and y2 eq 18 may be rearranged, resulting in eq 20. If $b_{y1} = b_{y2}$ it follows that

$$(\log k_{CF_3,y1} - \log k_{CH_3,y1}) - (\log k_{CF_3,y2} - \log k_{CH_3,y2}) = \frac{b_{y1} - b_{y2}}{0.059}(E_0^{CF_3} - E_0^{CH_3}) \qquad (20)$$

there is no reactivity difference for the reductions of the μ-acetato and the μ-(trifluoroacetato) complexes by two different reductants y1 and y2. In this case it would be meaningless to talk about the "selectivity" of a given reductant.

Figure 8 shows that an excellent linear correlation exists between the selectivity of a reductant y and its half-wave potential E_0^y[23] (eq 21). The stronger the reducing ability of

$$\log k_{CF_3,y} - \log k_{CH_3,y} = \log k_{et}^{CF_3,y} - \log k_{et}^{CH_3,y} = (0.95 \pm 0.02)E_0^{y} + (1.02 \pm 0.06) \qquad (21)$$

the reductant (or the more negative the free energy of the reaction) the smaller is the selectivity for the reductions of the series of μ-(acetato)-dicobalt(III) complexes by this reductant.

Guenther and Linck[24] have reported a similar observation—although on a less quantitative basis—that the selectivity of reductions of chlorocobalt(III) complexes by $[V(OH_2)_6]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ decreases with increasing negative free-energy change of the reaction. Other examples are given in ref 25. An analogous correlation is found by using Sykes' data[26] between the reactivity differences of reductions of $[Co(NH_3)_6]^{3+}$ and the superoxo complex $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ by Eu(II), Cr(II), V(II), and Ru(II), respectively, and the potentials, E_0^{redn}, of the latter.[40] This is shown in Figure 9. The differences of reactivities in this example span many orders of magnitude.[38]

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(22) Linck[24] as well as Endicott[15] used the expression "sensitivity". We prefer "selectivity" since this represents a well-established concept in physical organic chemistry where the difference of reactivities is called selectivity (see ref 28).

(23) The reduction potential for the couple $[Ti(dipic)_2]^-/[Ti(dipic)_2]^0$ is not known. From the measured selectivity (Table III) it is possible to estimate this potential to be +0.13 V (Figure 8).

(24) Guenther, P. R.; Linck, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 3769.

(25) (a) Dulz, G.; Sutin, N. *Inorg. Chem.* **1963**, *2*, 917. (b) Diebler, H.; Sutin, N. *J. Phys. Chem.* **1964**, *68*, 174.

(26) Hand, T. D.; Hyde, M. R.; Sykes, A. G. *Inorg. Chem.* **1975**, *14*, 1720.

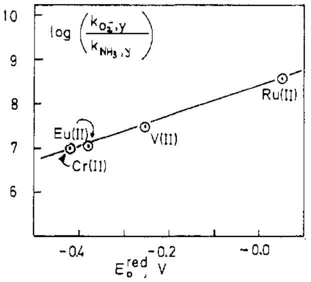

Figure 9. Correlation of the selectivity of outer-sphere reductions of two complexes of cobalt(III), a and b, by a common reductant y {$[Eu(OH_2)_6]^{2+}$, $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Ru(NH_3)_6]^{2+}$} vs. the normal reduction potentials, E_0^{redn}, of the respective reductant y {a = $[Co(NH_3)_6]^{3+}$, b = $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$}. Second-order rate constants, $k_{NH_3,y}$ and $k_{O_2^-,y}$ were taken from ref 26.

These findings *cannot* be interpreted as a manifestation of the Hammond postulate[27] and the validity of the reactivity–selectivity principle[24,28] in outer-sphere electron-transfer reactions because the reactivity within the precursor complexes does *not* increase linearly with increasing reduction potential of the reductant involved. For example, the rates for the reductions with the strong reductant $[Cr(OH_2)_6]^{2+}$ are slower than those observed for the weaker $[V(OH_2)_6]^{2+}$. This cannot be due to differences in the encounter complex formation constants since both reductants have a 2+ charge.

(c) log $k_{x,y1}$ – log $k_{x,y2}$ Correlations of Outer-Sphere Rates. Linck and co-workers[24,29,30] have proposed that the logarithms of the second-order rate constants $k_{x,y1}$ and $k_{x,y2}$ for outer-sphere reductions of a cobalt(III) complex x by two reductants y1 and y2 are linearly[39] related by eq 22. During the past

$$\log k_{x,y1} = \alpha \log k_{x,y2} + \beta \tag{22}$$

decade these log–log plots have mainly served as a diagnostic tool to assign outer-sphere mechanisms to the reduction of a Co(III) complex of interest by various reductants such as $[Ru(NH_3)_6]^{2+}$ and the aquo ions of Cr(II), V(II), Eu(II), and Ti(III).[8a,31-35] When such log–log plots are discussed, care must be taken to avoid confusion with correlations which are formally of the same type as eq 22 but where one set of reductions is of the inner-sphere type.[24] There are also known examples where both reductants follow the inner-sphere mechanism.[8a] We shall confine the following discussion to outer-sphere reactions and the log–log plots thereof. In order to systematize and analyze the log–log plots reported in the literature and in this work (Table IV), we propose that the log $k_{x,y}$ values pertaining to the stronger of the two reductants (i.e., the one with the more negative potential, E_0^y) should be written on the left-hand side of eq 22.

Table IV. log–log Correlations for Outer-Sphere Reductions of Cobalt(III) Complexes: $\log k_{y_1} = \alpha \log k_{y_2} + \beta^a$

y1, y2	α	β	$r^{2\,b}$	$\lvert E_0^{y_1} - E_0^{y_2}\rvert$,^{c} V
Cr, V	0.80 (3)	−1.86 (3)	0.996	0.145
	0.91^d	−1.7		
	0.98^e	−1.7		
Cr, Ru	0.55 (4)	−2.02 (4)	0.986	0.45
	0.95^f	−2.19		
Cr, Ti	0.56 (1)	−2.71 (1)	0.998	0.53
Cr, Fe	0.49 (1)	−1.92 (2)	0.999	0.68
V, Ru	0.68 (8)	−0.20 (8)	0.976	0.31
	0.64 (6)^g	−0.48 (15)	0.967	
	0.71 (5)^h	−0.76 (16)	0.966	
	0.95	−0.46		
V, Ti	0.69 (4)	−1.07 (2)	0.992	0.385
V, Fe	0.62 (2)	−0.07 (2)	0.998	0.53
Ru, Ti	1.00 (6)	−1.27 (3)	0.993	0.08
Ru, Fe	0.89 (7)	0.17 (11)	0.983	0.23
Ti, Fe	0.89 (3)	+1.43 (4)	0.998	0.15

^{a} y1 and y2 are two different reductants. These reductants are $[Cr(OH_2)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, $[Ti(dipic)_2]^-$, $[Ru(NH_3)_6]^{2-}$, and $[Fe(dipic)_2]^{2-}$. ^{b} Correlation factor. ^{c} Reduction potentials (E_0^Y) were taken from: Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* 1977, *99*, 5615 and references therein. The potential for the couple $[Ti(dipic)_2]^-/[Ti(dipic)_2]^0$ was estimated to be +0.13 V from Figure 7 of this work; the $[Fe(dipic)_2]^{2-}/[Fe(dipic)_2]^-$ reduction potential is +0.278 V: Anderegg, G. *Helv. Chim. Acta* 1960, *43*, 1530. ^{d} Reference 8a. ^{e} Reference 33. ^{f} Reference 31. ^{g} Reference 24 (not calculated previously). ^{h} Reference 35 (not calculated previously).

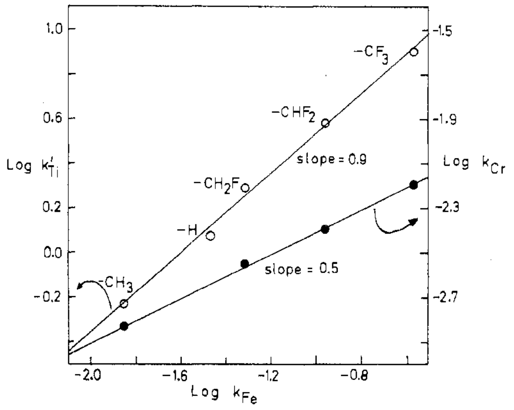

Figure 10. log–log correlations comparing the outer-sphere reductions of a series of μ-(acetato)-dicobalt(III) complexes by $[Ti(dipic)_2]^-$, $[Fe(dipic)_2]^{2-}$, and $[Cr(OH_2)_6]^{2+}$, respectively (eq 22).

Although no systematic exploration of the inherent potential of eq 22 has been undertaken to date it has been proposed that the slope α of these plots is close to unity for outer-sphere reactions involving Cr(II), V(II), Eu(II), and $[Ru(NH_3)_6]^{2+}$.[31-34] This would be in agreement with the simple Marcus cross relation. Only few gross deviations have been reported for log–log plots with $Ti(OH_2)_5OH^{2+}$ being one of the reductants.[34,35] A scrutiny of published data in conjunction with our results reveals that deviations from a slope of unity appear to be rather frequent. An unexpected result is that for the log k_V vs. log k_{Ru} plot {$[V(OH_2)_6]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ are reductants} *five* different values for α can be assembled from the literature by using Linck's data[24] (α = 0.64 (6) for the reductions of a series of chloroaminecobalt(III) complexes); Sykes' values from ref 35 yield α = 0.71 (5); Gould[31] reports a linear correlation with α = 0.95; finally, Sykes[36] reports a

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(37) On the other hand, it is noted that arguments based on the simple Marcus cross relation are not rigorously correct for reactions which are unsymmetrical with respect to charge and for reactions involving nonspherical reactants (e.g., μ-(carboxylato)-dicobalt(III) complexes).

(38) The slopes of Figures 8 (0.95) and 9 (3.33) are different. This may be due to the fact that the rate-determining step of the outer-sphere reduction of the binuclear μ-superoxo complex (Figure 9) does not involve reduction of a cobalt(III) center but the reduction of the μ-O_2^- bridge to a μ-O_2^{2-} bridge. It is also conceivable—as reviewer 1 has pointed out—that the differences in E_0^{ox} for the oxidants in Figures 8 and 9 (~0.1 V for the former and ~0.7 V for the latter) may account for this effect because nonlinearities are predicted by Marcus to be more important for the latter than the former.

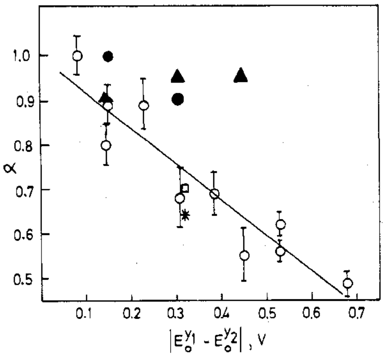

Figure 11. Correlation between the slope α of the log–log plots (eq 22) and the difference of normal reduction potentials of the involved reductants: ○, values obtained in this work for the reductions of binuclear μ-(acetato)-dicobalt(III) complexes (error bars represent the standard deviations) (the straight line was calculated by use of these values only); ▲, values taken from ref 8a and 31 for the outer-sphere reductions of a series of mononuclear complexes of cobalt(III); □, ref 35 (outer-sphere reduction of mononuclear and binuclear Co(III) complexes); *, ref 24 (outer-sphere reduction of chlorocobalt(III) complexes); ●, ref 36.

value $\alpha = 0.89$, and we find for the reductions of our dicobalt(III) complexes $\alpha = 0.68$ (9).

In Table IV all possible combinations of log $k_{x,y1}$ vs. log $k_{x,y2}$ correlations for the reductions of μ-(acetato)-dicobalt(III) complexes are summarized; where at hand, the respective values from the literature have been included. Figure 10 demonstrates the good linearity for log k'_{Ti} vs. log k_{Fe} and the log k_{Cr} vs. log k_{Fe} plots which yield slopes of 0.9 and 0.5, respectively. The range of log $k_{x,y}$ values for a reductant y is admittedly rather small. Nonetheless, it is immediately clear that α ranges from 0.49 to 1.0.

Figure 11 indicates that a linear correlation exists between the slope α of the log–log plots, eq 22, *and the difference of normal reduction potentials of the two involved reductants*, $|E_0^{y1} - E_0^{y2}|$. Only the values of α which were determined from the reductions of μ-(acetato)-dicobalt(III) complexes were used for the calculation of the straight line in Figure 11 (the correlation factor is 0.87 which is poor). (See eq 23.) From this

$$\alpha = -(0.8 \pm 0.1)|E_0^{y1} - E_0^{y2}| + (1.00 \pm 0.04) \quad (23)$$

correlation it follows that the slope α will be close to unity if the reduction potentials of the two reductants compared are similar and it will decrease with increasing dissimilarity of potentials.

According to eq 21 the difference of two selectivities for reductants y1 and y2 may be expressed as in eq 24. Eq 24

$$(\log k_{CF_3,y} - \log k_{CH_3,y1}) - (\log k_{CF_3,y2} - \log k_{CH_3,y2}) = 0.95(E_0^{y1} - E_0^{y2}) \quad (24)$$

combined with eq 23 and rearranged gives eq 25. Thus α is

$$(\log k_{CF_3,y1} - \log k_{CH_3,y1}) - (\log k_{CF_3,y2} - \log k_{CH_3,y2}) = 1.19(1 - \alpha) \quad (25)$$

a measure for the difference of selectivities of two reductants y1 and y2. If $\alpha = 1$, the two reductants will exhibit the same selectivity toward a series of dicobalt(III) oxidants which will be the case if y1 and y2 have similar reduction potentials. The reduction potentials of the aquo ions of Cr(II), Eu(II), and V(II) are relatively similar, and α values close to unity are in agreement with the above correlation. For the log k_V vs. log k_{Ru} plot, on the other hand, the difference of reduction potentials is 0.3 V, and α values reported in the literature vary from 0.64 to 0.95. The most serious violation of eq 23 is reported by Gould:[31] log k_{Cr} = 0.95 log k_{Ru} − 2.19 for the unambiguously outer-sphere reductions of a series of mononuclear complexes of cobalt(III). Since $E_0^{Cr} - E_0^{Ru} = 0.45$, a value for α of ~0.65 is predicted by eq 23.

Therefore, eq 23 cannot be of general validity and represents a special facet of our particular system. Most probably this kind of relation can only be found in reductions of amminecobalt(III) complexes.

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Registry No. $[Co^{III}{}_2]^{3+}$ (R = naphthyl), 74808-57-4; $[Co^{III}{}_2]^{3+}$ (R = quinolinyl), 74808-58-5; $[Co^{III}{}_2]^{3+}$ (R = pyridyl), 52375-40-3; $[Co^{III}{}_2]^{3+}$ (R = CH_3), 46240-70-4; $[Co^{III}{}_2]^{3+}$ (R = CH_2F), 46362-08-7; $[Co^{III}{}_2]^{3+}$ (R = CHF_2), 46470-29-5; $[Co^{III}{}_2]^{3+}$ (R = CF_3), 46753-32-6; $[Co^{III}{}_2]^{3+}$ (R = H), 46140-49-2; $[Fe(dipic)_2]^{2-}$, 71605-20-4; $Cr(OH_2)_6{}^{2+}$, 20574-26-9; $V(OH_2)_6{}^{2+}$, 15696-18-1; $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $[Ti(dipic)_2]^-$, 74808-59-6.

Supplementary Material Available: Tables of the observed pseudo-first-order rate constants for the reductions of binuclear μ-carboxylato complexes by $[Fe(dipic)_2]^{2-}$, $[Ti(dipic)_2]^-$, $[Ru(NH_3)_6]^{2+}$, $[V(OH_2)_6]^{2+}$, and $[Cr(OH_2)_6]^{2+}$ (3 pages). Ordering information is given on any current masthead page.

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(39) It is noted that the Marcus approach does not necessarily predict a linear correlation of log $k_{x,y1}$ with log $k_{x,y2}$ and some of the noted selectivities may only reflect the differences in curvature of $\Delta G^\ddagger = (\lambda/4)(1 + (\Delta G^\circ/\lambda))^2$ for different ranges of driving force and reorganizational parameters, as reviewer 1 has pointed out.

(40) A third example has been found for the oxidants $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5OH_2]^{3+}$: Huck, H.-M.; Wieghardt, K. *Angew. Chem.* **1980**, *92*, 580; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 558.