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Thermal Intramolecular Cobalt(III)–Iron(II) and Cobalt(III)–Titanium(III) Electron-Transfer Reactions Involving Outer-Sphere and Inner-Sphere Precursor Complexes

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Two binuclear cobalt(III) complexes containing a μ-[pyridine-4-carboxylato(*O,O'*)-2,6-dicarboxylate] bridge (**1**, **2**) react rapidly with $[Fe(OH_2)_6]^{2+}$ and $[Ti(OH_2)_6]^{3+}$, respectively, to form 1:1 complexes ($[Co^{III}{}_2–L–M(OH_2)_3]$, L = bridging ligand, M = Fe(II) and Ti(III)) at pH 2–3 and 2:1 complexes ($[Co^{III}{}_2–L–M–L–Co^{III}{}_2]$, M = Fe(II) and Ti(III)) at pH >4. Intramolecular rate constants for the one-electron transfer (ET) within the inner-sphere precursor complexes containing a Ti(III) center have been measured. No influence of the differing oxidizing abilities of the Co(III) centers (the nonbridging NH_3 ligands of **1** are substituted by 1,4,7-triazacyclononane in **2**) on the intramolecular reaction rate has been observed; alteration of the reducing power of Ti(III) in going from 1:1 to 2:1 complexes **6**, **7** and **8**, **9** exhibits a marked effect. This behavior is interpreted in terms of a "chemical" (two-step) mechanism: formation of a radical intermediate (i.e., the reduced bridging ligand) is considered to be the rate-determining step. In contrast, the transient 2:1 precursor complex **4** (Fe(II) being the weaker reductant) appears to react via resonance transfer. Outer-sphere reductions of some binuclear μ-carboxylato-cobalt(III) complexes by $[Fe(dipic)_2]^{2-}$ or $[Ti(dipic)_2]^-$ (dipic = pyridine-2,6-dicarboxylate) have also been studied. An outer-sphere association constant, K_o, and an intramolecular ET rate constant, k_{et}, have been determined for the reduction of the μ-(pyridine-4-carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)] cation by $[Fe(dipic)_2]^{2-}$ (74 M^{-1}, 3.7×10^{-3} s^{-1} at 25 °C; $\mu = 0.1$ M). No difference in the reactivity of the outer-sphere (ion-pair) precursor complex and the structurally very similar inner-sphere precursor complex **4** is observed. This is taken as evidence that the uninterrupted bond system from Fe(II) to Co(III) in **4** does not provide a favorable electron pathway. A resonance transfer exhibiting the characteristics of an outer-sphere process is proposed for the intramolecular ET within **4**. In contrast, outer-sphere reductions of binuclear Co(III) complexes by $[Ti(dipic)_2]^-$ via ion-pair precursor complexes are shown to be less favorable than the corresponding intramolecular ET within the inner-sphere complexes **8** and **9**.

Introduction

The mechanism of thermal intramolecular electron transport between two metal ions which are connected by chemical bonds via an organic bridging ligand within a binuclear complex (inner-sphere precursor complex) has been conceptualized in terms of a "two-step" or "chemical" mechanism or, alternatively, a resonance transfer.[1,2] The former mechanism implies the transient reduction of the organic bridging ligand and formation of an intermediate radical species, whereas in the latter case no intermediates are thought to be generated.[3] The "radical-ion" mechanism may be formulated as

$$A^{III}LB^{II} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^{III}\dot{L}B^{III}$$

$$A^{III}\dot{L}B^{III} \xrightarrow{k_2} A^{II}LB^{III} \xrightarrow{\text{rapid}} \text{products}$$

A, B = transition metals; L = organic bridging ligand

Radical intermediates of the proposed type have been directly observed in only very few instances with strong reductants such as $[Cr(OH_2)_6]^{2+}$ [4] or the hydrated electron.[5] The observed first-order rate constant for the intramolecular ET can represent two limiting situations according to the above scheme by assuming the steady-state approximation to be valid for the concentration of the radical intermediate. If $k_{-1} \gg k_2$, then $k_{obsd} = (k_1/k_{-1})k_2$, but if $k_2 \gg k_{-1}$, then $k_{obsd} = k_1$; i.e., the formation of the radical intermediate is rate determining. The first limiting case should lead to a marked dependence of the rate on both the oxidizing power of the oxidant and the reducing ability of the reductant, whereas in the latter case only a marginal influence of the oxidizing transition-metal ion is expected—provided the oxidant does not change the reducibility of the bridging ligand greatly. It is noted that for a resonance-transfer mechanism a dependence of the intramolecular ET rate on the nature of the oxidant *and* the reductant is predicted. This mechanistic possibility is kinetically not distinguishable from the first limiting case of the chemical mechanism.

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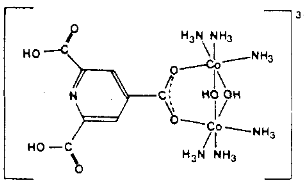
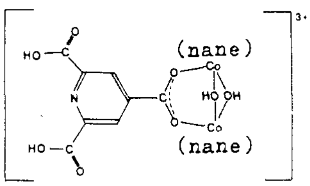
In the present study we have prepared two binuclear cobalt(III) complexes which undergo intramolecular ET reactions with Fe(II) and Ti(III). The oxidizing ability of the cobalt(III) ions is altered by merely varying the nature of the nonbridging ligands (NH_3 ligands are substituted by a cyclic secondary amine). Complexes **1** and **2** can be looked at as tridentate chelating ligands.[20] The kinetics of the reductions of **1** and **2** with $[Fe(OH_2)_6]^{2+}$ and $[Ti(OH_2)_6]^{3+}$, respectively, at various pH values are described in this paper.

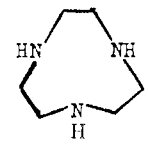


1

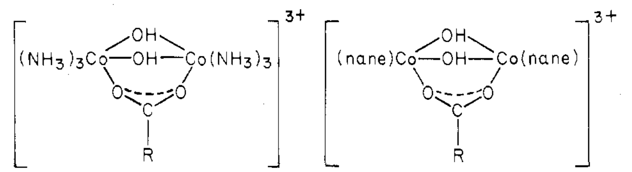


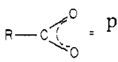
2

nane = 1,4,7-triazacyclononane



Intramolecular ET reactions of transition-metal ions (predominantly of Co(III) and Fe(II)) via *outer-sphere* precursor complexes (no common covalent bond between the first coordination spheres of the reactants exists during the act of ET) have been studied in some detail in the past.[6,7] It is important to measure intramolecular ET rate constants of structurally very similar complexes which can react via inner-sphere precursor complexes.[8,29] Such a system would be ideally suited to "test" electron permeabilities[9] of individual covalent bonds within the electron-mediating moiety: Is ET more favorable if it is mediated by an uninterrupted covalent bond system from the oxidizing to the reducing transition-metal center or if it proceeds by an outer-sphere mechanism which lacks only one distinct covalent bond between the reactants? Therefore, reductions of several binuclear μ-carboxylato cobalt(III) complexes by $[Fe(dipic)_2]^{2-}$ and $[Ti(dipic)_2]^-$, respectively, have been studied (dipic = pyridine-2,6-carboxylate).



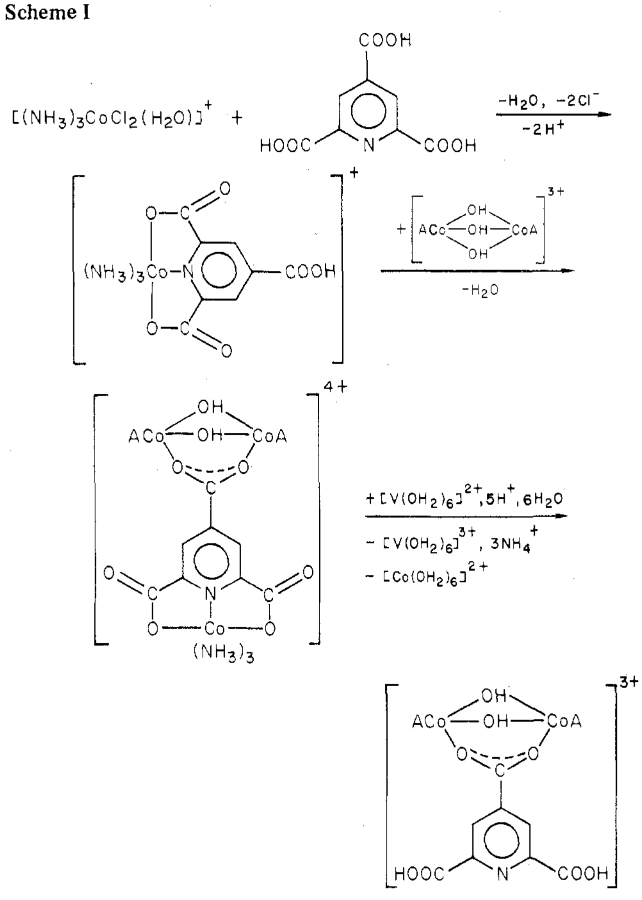
 = pyridine-4-carboxylate, pyrazinecarboxylate, benzoate, or acetate

Experimental Section

Materials. Pyridine-2,6-dicarboxylic acid (Merck) was used as received. Pyridine-2,4,6-tricarboxylic acid was prepared from 2,4,6-trimethylpyridine by oxidation with $KMnO_4$.[10] Buffer solutions were prepared by adding 0.1 M HCl to a 0.1 M aqueous solution of glycine (pH 2–3) or by adding 0.1 M NaOH to acetic acid (0.1 M) (pH 4–5) until the desired pH was reached. 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. Stock solutions of $[Ti(OH_2)_6]^{3+}$ in HCl were prepared by dissolving titanium hydride (Fluka) in 1 M HCl at 50 °C (~60 h) or in order to avoid the presence of chloride ions in *p*-toluenesulfonic acid under air-free conditions. Solutions containing $[V(OH_2)_6]^{2+}$ in perchloric acid were prepared by electrolytic reduction of solutions of vanadium(IV) perchlorate. Deionized water was distilled and then used for kinetic experiments.

Preparation of Complexes. $[(NH_3)_3CoCl_2(OH_2)]Cl$ and $[(NH_3)_3Co(OH)_3Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$ were prepared following the literature procedure.[11] Preparation of the binuclear $[(nane)Co(OH)_3Co(nane)](ClO_4)_3$ complex (nane = 1,4,7-triazacyclononane) will be described elsewhere.[12] The complexes **1** and **2** containing a μ-[2,6-dicarboxypyridine-4-carboxylato(*O,O'*)] bridging ligand were prepared according to Scheme I which involves the selective inner-sphere reduction of one cobalt(III) center of two trinuclear complexes, respectively, with $[V(OH_2)_6]^{2+}$ as reductant.

Scheme I



A = $3NH_3$ or 1,4,7-triazacyclononane

[(4-Carboxypyridine-2,6-dicarboxylato)triamminecobalt(III)] Perchlorate. $[Co(NH_3)_3(OH_2)Cl_2]Cl$ (7.0 g) and pyridine-2,4,6-tricarboxylic acid (7.0 g) were dissolved in 120 mL of 1 M perchloric acid at 70 °C. The solution was filtered while still warm. When the solution was cooled (2 °C), violet crystals precipitated which were filtered off. The crude product was dissolved in a minimum amount of 1.5 M perchloric acid at 50 °C and precipitated with concentrated $HClO_4$ at 2 °C. The crystals were washed with ethanol and ether and air-dried. Anal. Calcd for $[Co(NH_3)_3(C_8H_3O_6N)](ClO_4)$: C, 22.96; H, 2.90; N, 13.38; Co, 14.10. Found: C, 23.2; H, 2.9; N, 13.6; Co, 14.4.

μ-[[Pyridine-4-carboxylato(*O,O'*)-2,6-dicarboxylato]triamminecobalt(III)]-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate. A suspension of (4-carboxypyridine-2,6-dicarboxylato)triamminecobalt(III) perchlorate (5.2 g) and of tri-μ-hydroxo-bis[triamminecobalt(III)] perchlorate (9.5 g) in 80 mL of 1 M perchloric acid was stirred at 70 °C for 15 min. To the filtered and cooled solution (5 °C) was added 5 mL of concentrated $HClO_4$. This solution was kept in a refrigerator overnight. Red-violet crystals were filtered off, washed with ethanol and ether and air-dried. Anal. Calcd for $[Co_3(NH_3)_9(OH)_2(C_8H_2O_6N)](ClO_4)_4 \cdot H_2O$: C, 9.73; H, 3.37; N, 14.18; Co, 17.90. Found: C, 9.7; H, 3.5; N, 14.2; Co, 18.0.

μ-[2,6-Dicarboxypyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] Perchlorate. To a solution of the trinuclear μ-[(pyridine-2,4,6-tricarboxylato)triamminecobalt(III)]-di-μ-hydroxo-bis[triamminecobalt(III)] perchlorate (1 mmol) in 50 mL of 0.2 M perchloric acid an equimolar amount of $[V(OH_2)_6]^{2+}$ in perchloric acid was added under strictly air-free conditions (argon atmosphere). The reactants were mixed by using syringe techniques at 25 °C. The color of the solution changed within 5 min from violet to red. A 110-mL sample of concentrated $HClO_4$ was then added. This solution was allowed to stand in an open vessel in a drafty fume cupboard for 3 days. Red crystals slowly precipitated which were filtered off, washed with ethanol and ether, and air-dried.

The visible absorption spectrum of this complex exhibits a maximum at 524 nm (ϵ 110 L mol^{-1} cm^{-1}) which is typical for all μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes.[13] The IR spectrum reveals the presence of uncomplexed protonated carboxylic groups (ν(C=O) 1730 cm^{-1}) and of a symmetrical[14] μ-carboxylato bridge (ν_{as}(C–O) 1555 cm^{-1}; ν_s(C–O) 1440 cm^{-1}). Anal. Calcd for $[Co_2(NH_3)_6(OH)_2(C_8H_4O_6N)](ClO_4)_3$: C, 12.60; H, 3.17; N, 12.86; Co, 15.46. Found: C, 12.5; H, 3.4; N, 13.1; Co, 15.1.

μ-[2,6-Dicarboxypyridine-4-carboxylato(*O,O′*)]-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] Perchlorate. Tri-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] perchlorate (4 g) and (4-carboxypyridine-2,6-dicarboxylato)triamminecobalt(III) perchlorate (1.6 g) were dissolved in 100 mL of 0.5 M perchloric acid at 60 °C. The temperature was maintained for 10 min. To the cooled and filtered solution were added equal amounts of ethanol and acetone dropwise until violet crystals precipitated. These were filtered off, washed with ethanol and ether, and air-dried. The crude product was used without further characterization. To a solution of this trinuclear complex (3 g, ~2.5 mmol) in 20 mL of degassed 1 M perchloric acid was added an equimolar quantity of $[V(OH_2)_6]^{2+}$ in perchloric acid under an argon atmosphere. After the selective reduction of the $(NH_3)_3Co^{III}$ entity is complete (~5 min at 25 °C), 5 mL of concentrated $HClO_4$ was added. The solution was allowed to stand in a drafty fume cupboard in an open vessel for 3 days. Red crystals precipitated slowly which could be recrystallized from 2 M $HClO_4$. The IR spectrum of the perchlorate salt again shows the presence of uncomplexed protonated carboxylic groups and a symmetrical μ-carboxylato(*O,O′*) bridge. The visible absorption spectrum exhibits a maximum at 513 nm (ϵ 190 L mol^{-1} cm^{-1}). Anal. Calcd for $[Co_2(C_{12}H_{30}N_6)(OH)_2(C_8H_4O_6N)](ClO_4)_3 \cdot 1.5H_2O$: C, 25.38; H, 4.16; N, 10.37; Co, 12.46. Found: C, 24.5; H, 4.2; N, 10.3; Co, 12.1.

(Pyridine-2,6-dicarboxylato)triaquotitanium(III) Chloride.[15] A slurry of dipicolinic acid (0.01 mol) and titanium trichloride (0.01 mol) in 30 mL of water was heated at 55 °C for 10 min under an argon atmosphere. Upon cooling (2 °C) of the filtered solution, red-brown crystals precipitated which were filtered off in air and washed with ethanol and ether. Anal. Calcd for $[Ti(C_7H_3O_4N)(OH_2)_3]Cl \cdot 2H_2O$: Ti, 14.10; Cl, 10.50; C, 24.83; H, 3.57; N, 4.13. Found: Ti, 13.8; Cl, 10.1; C, 25.4; H, 3.7; N, 4.2.

Cesium Bis(pyridine-2,6-dicarboxylato)titanate(III). $[Ti(OH_2)_6]^{3+}$ (0.01 mol) in HCl and disodium pyridine-2,6-dicarboxylate (0.023 mol) in 60 mL of water were allowed to react for 10 min at 35 °C under argon (the pH of this solution was adjusted to 6). To the cooled solution (5 °C) was added solid Cs_2SO_4 until blue crystals precipitated which were filtered off under argon and washed with deoxygenated ethanol and ether. The solid must be kept under an inert atmosphere since the crystals are air sensitive. Anal. Calcd for $Cs[Ti(C_7H_3O_4N)_2] \cdot 3H_2O$: Cs, 23.52; C, 29.76; H, 2.14; N, 4.96. Found: Cs, 21.8; C, 29.5; H, 2.2; N, 5.1.

Barium Bis(pyridine-2,6-dicarboxylato)ferrate(II). Dipicolinic acid (0.84 g) was dissolved in 50 mL of water. The pH of this solution was adjusted to 6 by adding 1 M NaOH. A 5-mL sample of an aqueous solution of $Fe(ClO_4)_2$ (0.5 M) was added under an argon atmosphere. The color of the solution became red-brown. A 0.6-g sample of $BaCl_2 \cdot 2H_2O$ was added. Precipitation was initiated by adding ethanol dropwise until the solution became turbid. After the solution stood for 2 days in the refrigerator, red-brown crystals of the desired product were filtered off, washed with ethanol and ether, and air-dried. The dry solid product is air stable. Anal. Calcd for $Ba[Fe(C_7H_3O_4N)_2] \cdot 5H_2O$: Ba, 22.40; C, 27.40; H, 2.63; N, 4.57. Found: Ba, 21.9; C, 27.9; H, 2.5; N, 4.7.

μ-[Pyridine-4-carboxylato(*O,O′*)-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] Perchlorate. Tri-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] perchlorate (2 g) and pyridine-4-carboxylic acid (0.4 g) were dissolved in 50 mL of perchloric acid (1.0 M). The temperature was maintained at 55 °C for 10 min during which time the color changed from violet to red. Ethanol was added dropwise to the cooled solution (5 °C) until the solution became turbid. After the solution stood for 12 h in the refrigerator, red crystals were filtered off, washed with ethanol and ether, and air-dried. The pyridine nitrogen atom is protonated under these conditions. The visible absorption spectrum exhibits a maximum at 513 nm (ϵ 185 L mol^{-1} cm^{-1}). Anal. Calcd for $[Co_2(C_6H_{15}N_3)_2(OH)_2(C_6H_5NO_2)](ClO_4)_4$: Co, 12.66; C, 23.22; H, 4.01; N, 10.53. Found: Co, 12.7; C, 23.7; H, 4.1; N, 10.5.

Rate Measurements. The rates of the reactions of complexes **1** and **2** with $[Ti(OH_2)_6]^{3+}$, respectively, were studied on a Durrum stopped-flow spectrophotometer, Model 110, at 560 nm. Since the employed Ti(III) concentrations were small (~0.7 × 10^{-4} M), great care was exercised to ensure that the flow system was free of traces of oxygen by flushing it with acidic solutions of $[Cr(OH_2)_6]^{2+}$ and degassed, distilled water prior to the experiments with Ti(III). Kinetic runs were carried out under pseudo-first-order conditions with an excess of the respective oxidant. At increasing pH, the solubility of **1** and **2** decreases (maximum [complex] = 2 × 10^{-3} M at pH 6, 25 °C, μ = 0.1 M). It has therefore not been possible to vary the complex concentration over as wide a range as would have been desirable (in the case of complex **2** a factor of 3 has been accomplished). Solutions containing the oxidants **1** and **2**, respectively, in the appropriate buffer were mixed with solutions of $[Ti(OH_2)_6]^{3+}$ in aqueous HCl (10^{-3} M). Only the second stage of the reaction (decrease in absorbance; vide infra) has been followed in all experiments. Transmittance vs. time curves were obtained from photographs of storage oscilloscope traces. First-order rate constants were evaluated from gradients of plots of ln ($A_t - A_\infty$) against time, where A_t is the absorbance at time *t* and A_∞ that after the reaction is complete. At higher pH values (>4) the quality of such measurements was deteriorating, and the reproducibility of replicate runs was in some cases not better than 20%. Plots of ln ($A_t - A_\infty$) against time were then linear for 2–3 half-lives.

The rates of the outer-sphere reductions of binuclear cobalt(III) complexes by $[Fe(dipic)_2]^{2-}$ and $[Ti(dipic)_2]^-$, respectively, were measured under pseudo-first-order conditions (excess oxidants) by using conventional spectrophotometric methods on a UNICAM SP 1700 spectrophotometer. In general, the reductants $[Fe(dipic)_2]^{2-}$ and $[Ti(dipic)_2]^-$ were generated in situ according to the following procedure. Aliquot volumes of $[Fe(OH_2)_6]^{2+}$ or $[Ti(OH_2)_6]^{3+}$ (1 × 10^{-4} M) in an aqueous solution of dipicolinic acid (0.01 M) and the respective oxidant (0.5–5.0 × 10^{-3} M) dissolved in an acetate buffer (0.2 M, pH 5.0) were mixed under an argon atmosphere by using standard syringe techniques. Under these conditions the formation of the reductants is rapid and quantitative (the rates of reductions are independent of uncomplexed dipicolinic acid concentrations and pHs of 4.0–5.5). Decreases of absorbance were followed at 525 nm (Fe(II) being the reductant) and at 600 nm for the Ti(III) reductions. First-order rate constants were obtained from plots of ln ($A_t - A_\infty$) vs. time which were linear for ca. 5 half-lives.

All reductions reported in this paper involve purely *thermal* electron transfer. We have found no indication for light-induced ET reactions.[16]

Results

Preliminary Observations. Both the pyridine-2,6-dicarboxylic acid (dipicolinic acid, dipic) and the pyridine-2,4,6-tricarboxylic acid are tridentate chelating ligands and are known to coordinate to transition-metal aquo ions in the +2 and +3 oxidation states forming 1:1 and 1:2 complexes.[17,18] Reaction of dipicolinic acid with $[Ti(OH_2)_6]^{3+}$ in hydrochloric acid (pH 1–3) under an argon atmosphere yields a brown cationic complex, $[Ti(dipic)(OH_2)_3]^+$, which can be isolated as the chloride salt.[15] The UV spectrum exhibits an absorption maximum at 490 nm (ϵ 625 L mol^{-1} cm^{-1}). At higher pH values (4–6) and excess dipicolinic acid the blue 1:2 complex, $[Ti(dipic)_2]^-$, is formed which precipitates upon addition of Cs_2SO_4 as the cesium salt (λ_{max} 513 nm, ϵ 1.1 × 10^3 L mol^{-1} cm^{-1}).

The same behavior is deduced for solutions containing $[Ti(OH_2)_6]^{3+}$ and pyridine-2,4,6-tricarboxylic acid. Figure 1 shows the absorption at 575 nm of a solution of Ti(III) and the organic ligand as a function of pH. At pH 2–3 the 1:1 complex (λ_{max} 575 nm, ϵ 1.3 × 10^3 L mol^{-1} cm^{-1}) is the predominant species formed (this was confirmed by a Job plot), whereas at higher pH values (4.5–6.0) the 1:2 complex (λ_{max} 562 nm, ϵ 1.5 × 10^3 L mol^{-1} cm^{-1}) is stable.

With dipicolinic acid at pH >4, $[Fe(OH_2)_6]^{2+}$ forms an intensely colored complex (1:2) which can be isolated as the barium salt (λ_{max} 480 nm, ϵ 1.9 × 10^3 L mol^{-1} cm^{-1}). The pH dependence of the absorption of solutions containing $[Fe(OH_2)_6]^{2+}$ and pyridine-2,4,6-tricarboxylic acid (Figure 1) indicates the formation of a 1:1 complex at low pH and a 1:2

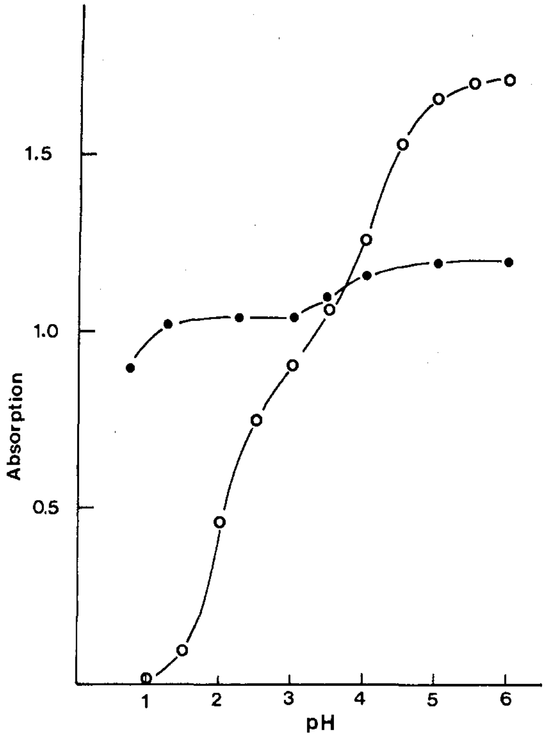
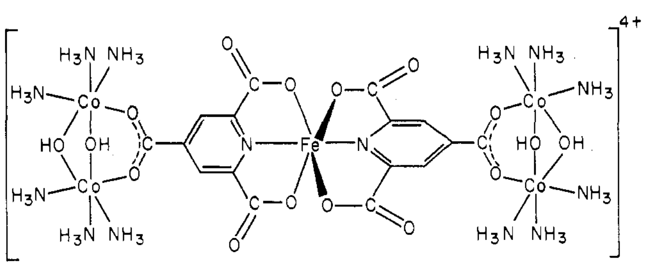


Figure 1. pH dependence at 25 °C of the absorption at 500 nm of buffered solutions (pH 1–3.5, glycine/HCl; pH 4–6 acetic acid/NaOH) of pyridine-2,4,6-tricarboxylic acid (6 × 10^{-4} M) and $[Fe(OH_2)_6]^{2+}$ (○, 2 × 10^{-4} M) or $[Ti(OH_2)_6]^{3+}$ (●, 2 × 10^{-4} M, followed at 575 nm).

complex (λ_{max} 515 nm, ϵ 2.2 × 10^3 L mol^{-1} cm^{-1}) at high pH values.

Reactions of Binuclear μ-[[2,6-Dicarboxypyridine-4-carboxylato(*O,O'*)]cobalt(III)] Complexes with $[Fe(OH_2)_6]^{2+}$. In a preliminary communication we have reported[19] the rapid formation of a 1:1 complex[20] of **1** and $[Fe(OH_2)_6]^{2+}$ in acidic aqueous solution (pH 1.5–2.5). No reduction of cobalt(III) has been observed; the potential redox precursor complex is stable. At pH >4 and excess of **1** over Fe(II), the corresponding 2:1 complex **4** is formed which undergoes an intramolecular ET reaction, eq 1 and 2, generating one Co(II) and one Fe(III) ion per complex cation **4**. The cation **4** is a precursor complex of the inner-sphere type; oxidant (Co(III)) and reductant (Fe(II)) are connected by covalent bonds via an organic bridging ligand.

$$2\,\mathbf{1} + [Fe(OH_2)_6]^{2+} \rightleftharpoons 4H^+ + 6H_2O +$$



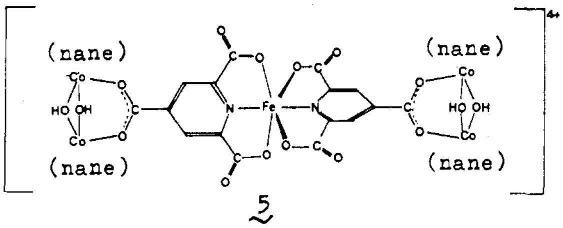
4

(1)

$$[Co^{III}{}_2LFe^{II}LCo^{III}{}_2]^{4+} \xrightarrow{k_{et}} [Co^{III}Co^{II}LFe^{III}LCo^{III}{}_2]^{4+} \xrightarrow{\text{rapid}} \text{products} \quad (2)$$

In labile systems, the formation of a precursor complex gives, in general, no assurance that the ET occurs within this complex. An equally plausible mechanism involves dissociation of the precursor complex in the rate-determining step followed by fast outer-sphere ET. This mechanism cannot be operative in our systems because the probable dissociation products of **4** (a 1:1 complex and **1** or $[Fe(OH_2)_6]^{2+}$ and **1**) do not undergo redox reactions at all. The reducing ability of such dissociatively generated Fe(II) species does not suffice to reduce the Co(III) centers. Dissociation of OH-bridged cobalt(III) moieties has not been observed under our experimental conditions.

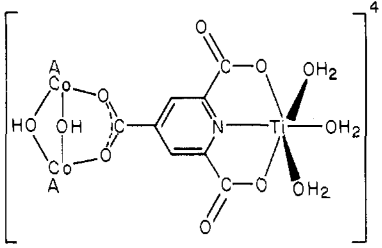
Upon substitution of the nonbridging ammonia ligands of **1** by the cyclic secondary amine 1,4,7-triazacyclononane, the binuclear complex **2** is obtained. With $[Fe(OH_2)_6]^{2+}$ **2** also reacts according to eq 1. In aqueous solutions (phthalate buffer, pH 6, μ = 0.04 M, 25 °C) of $[Fe(OH_2)_6]^{2+}$ (1 × 10^{-4} M) and of **2** ((2–8) × 10^{-4} M) the violet complex **5** is formed quantitatively (λ_{max} 540 nm, ϵ 2.5 × 10^3 L mol^{-1} cm^{-1}). But contrary to **4** no subsequent ET reaction is observed. No changes of the absorption spectrum of **5** could be detected for 48 h at 30 °C. Since the bridging structural units between Co(III) and Fe(II) in **4** and **5** are identical, a marked influence of the nonbridging ligands[21] coordinated to the oxidizing centers of Co(III) on the rate of intramolecular ET must be effective. It is known that substitution of NH_3 ligands coordinated to Co(III) by ethylenediamine reduces the oxidizing power of the cobalt(III) center substantially.[22] Therefore, the reduced driving force for ET of **5** as compared to **4** is thought to be responsible for the differing reactivities of these complexes.



5

Reactions of Binuclear μ-[[2,6-Dicarboxypyridine-4-carboxylato(*O,O'*)]cobalt(III)] Complexes with $[Ti(OH_2)_6]^{3+}$. When a solution of $[Ti(OH_2)_6]^{3+}$ (1 × 10^{-4}M) in a glycine buffer (pH 2–3) and solutions containing complexes **1** and **2**, respectively ((0.8–1.2) × 10^{-3} M), are mixed by stopped-flow techniques at 25 °C, a rapid increase in absorbance at 562 nm is observed during the first 10–50 ms which is followed by a slower decrease in absorbance. A first-order dependence on [complex] and [Ti(III)], respectively, and an inverse dependence on [H^+] have been established for the first step of the reaction. This is consistent with the formation of 1:1 inner-sphere precursor complexes according to eq 3. The uncomplexed ligand, dipicolinic acid, and $[Ti(OH_2)_6]^{3+}$ react under these conditions to afford $[(dipic)Ti(OH_2)_3]^+$. Substitution reactions of the $[Ti(OH_2)_6]^{3+}$ ion are known to be fast.[23]

$$\mathbf{1} \text{ or } \mathbf{2} + [Ti(OH_2)_6]^{3+} \overset{K_1}{\rightleftharpoons}$$



$$+ 3H_2O + 2H^+$$

6: A = $3NH_3$
7: A = 1,4,7-triazacyclononane

(3)

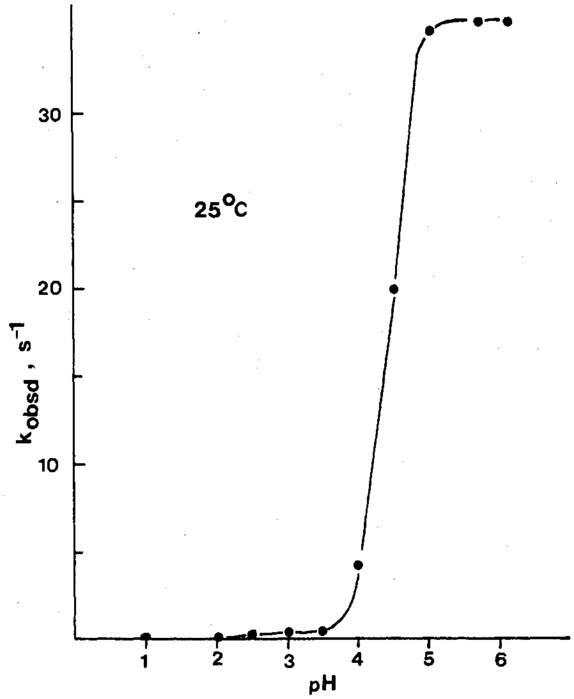


Figure 2. pH dependence of the first-order rate constant of the bleaching process, k_{obsd}, of solutions containing **1** (3×10^{-4} M) and $[Ti(OH_2)_6]^{3+}$ (0.4×10^{-4} M) at 25 °C (μ = 0.05 M). Buffers used: pH 1–3, glycine/HCl; pH 3.5–5, acetic acid/NaOH; pH 5–6, phthalic acid/NaOH.

The subsequent decomposition of **6** and **7** which is accompanied by a decrease in absorption at 562 nm yields one $[Co(OH_2)_6]^{2+}$ and one Ti(IV) ion per complex cation, eq 4.

$$\mathbf{6} \text{ or } \mathbf{7} \xrightarrow{k_{et}} [Co^{II}Co^{III}LTi^{IV}]^{4+} \xrightarrow{\text{rapid}} \text{products} \qquad (4)$$

The kinetics of this bleaching process have been measured by using pseudo-first-order conditions with **1** or **2** in excess ($(2–8) \times 10^{-4}$ M) over Ti(III) (0.3×10^{-4} M) at pH 2.2 and 3.1 (glycine buffer, μ = 0.01 M). Due to the low solubilities of **1** and **2**, their respective concentrations could not be varied over a wider range. Nevertheless, the observed first-order rate constants appear to be *independent* of the employed concentrations of **1** and **2** and of the pH. A mechanism involving rapid precursor complex formation at a constant pH, eq 3, and subsequent irreversible ET as the rate-determining step, eq 4, leads to a functional dependence of k_{obsd} as in eq 5. (It

$$k_{obsd} = \frac{k_{et}K_f[Co^{III}_2]}{1 + K_f[Co^{III}_2]} \qquad (5)$$

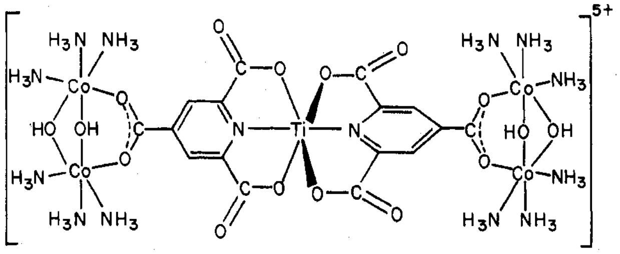
is noted that K_f is a complex function of $[H^+]$.) If the product K_f[complex] ≫ 1 at a given pH, eq 5 reduces to $k_{obsd} = k_{et}$. Stability constants for 1:1 complexes of trivalent metal–aquo ions with dipicolinic acid are known to be large.[18] Therefore, at pH values of 2–3 and complex concentrations of $\sim 10^{-4}$ M it is plausible that K_f[complex] ≫ 1, and the measured first-order rate constants are intramolecular ET rate constants. From the temperature dependence of k_{obsd}, activation parameters for the intramolecular ET of **6** and **7** have been evaluated (Table I).

At pH >4 and excess of **1** or **2** over Ti(III), formation of 2:1 precursor complexes can be expected by analogy with the behavior of Ti(III) and uncomplexed pyridine-2,4,6-tricarboxylic acid or dipicolinic acid (Figure 1). Indeed, the rate of the second stage of the reaction of **1** or **2** with $[Ti(OH_2)_6]^{3+}$ is dramatically enhanced at pH 3.5 and again reaches a constant value at pH >5. This is demonstrated qualitatively in Figure 2. The first stage of the reaction, i.e., formation of the precursor complex, is complete within mixing time of the stopped-flow experiment at pH >4 and cannot be observed.

Table I. Intramolecular Electron-Transfer Rate Constants and Respective Activation Parameters for the Inner-Sphere-Type Precursor Complexes **4–9**

precursor	t, °C	k_{et}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	ref
4	25	3.7×10^{-3}	24.0 ± 0.2	+11 ± 1	18
5	25	no ET reacn			this work
6	2.5	0.02	19 ± 1	+3 ± 3	this work
	15	0.11			
	25	0.25			
	35	0.95			
7	7	0.0025	18.5 ± 1	−4 ± 3	this work
	16	0.008			
	25	0.023			
	34	0.047			
8	7.5	8.5	14 ± 1	−6 ± 3	this work
	16	18.0			
	25	32.0			
	31.5	56.0			
	38	82.0			
9	8	3.1	15 ± 1	−2 ± 3	this work
	17.2	6.5			
	25	15.6			
	36	38.0			

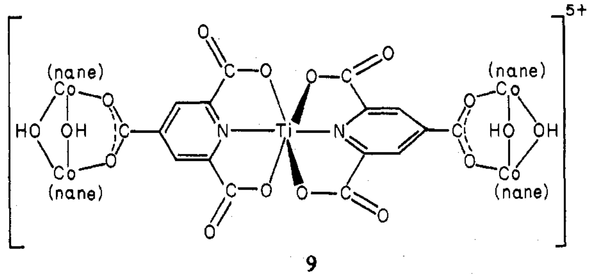
$$\mathbf{6} + \mathbf{1} \xrightleftharpoons{K_f}$$



8

$$+ \; 3H_2O + 2H^+ \qquad (6)$$

$$\mathbf{7} + \mathbf{2} \xrightleftharpoons{K_f}$$



9

$$+ \; 3H_2O + 2H^+ \qquad (7)$$

$$[Co^{III}_2LTi^{III}LCo^{III}_2]^{5+} \xrightarrow{k_{et}} [Co^{III}Co^{II}LTi^{IV}LCo^{III}_2]^{5+} \xrightarrow{\text{rapid}} \text{products} \qquad (8)$$

The rate of the decomposition of **8** is independent of the complex concentration ([**1**] = $(1.5–6.0) \times 10^{-4}$ M, [Ti(III)] = 0.3×10^{-4} M; pH 4.5–6.0 (acetate buffer), μ = 0.05 M) and of $[H^+]$. First-order rate constants, k_{et}, and activation parameters for the intramolecular ET within the precursor complex **8** are summarized in Table I.

For the reaction of **2** with $[Ti(OH_2)_6]^{3+}$ at pH 5.2 (acetate buffer, μ = 0.05 M) a slight nonlinear dependence of the rate of decomposition of **9** on **2** is observed (Table II). A reaction

Table II. Kinetic Data of the Reaction of **2** with Ti(III)[b]

t, °C	[**2**],[a] M	k_{obsd}, s^{-1}	*t*, °C	[**2**],[a] M	k_{obsd}, s^{-1}
8	1.5	1.8	25.0	1.5	6.0
	2.2	2.1		2.2	7.5
	3.3	2.3		3.3	9.1
17.2	1.5	3.3	35.8	2.2	14.0
	2.2	4.0		3.3	18.0
	3.3	4.6			

[a] Variation of [**2**] is small due to the very low solubility of **2** at pH >4. [b] [Ti(III)] = 3 × 10^{-5} M; pH 5.2, acetate buffer (μ = 0.05 M).

Table III. Kinetic Data for the Reduction of μ-[Pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)]$^{3+}$ and the μ-Acetato(*O,O'*) Analogue by [Fe(dipic)$_2$]$^{2-}$ [b]

t, °C	10^3 × [Co$^{III}_2$]	10^4 × k_{obsd}	complex
15	1.0	0.97	μ-(pyridine-4-carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)]
	2.0	1.76	
	5.0	3.32	
25	1.0	2.52	
	2.0	5.02	
	5.0	9.90	
35	1.0	6.47	
	2.0	12.1	
	3.5	21.8	
	5.0	27.0	
	8.0	39.0	
25	1.0	0.12	μ-acetato-di-μ-hydroxo-bis-[triamminecobalt(III)]
	2.0	0.26	
	4.0	0.52	
	10.1	1.32	
	15.1	1.98	

[a] μ = 0.2 M. [b] Concentration of [Fe(dipic)$_2$]$^{2-}$ 5 × 10^{-5} M; pH 4.6 (acetate buffer), 0.001 M dipicolinic acid (μ = 0.1 M).

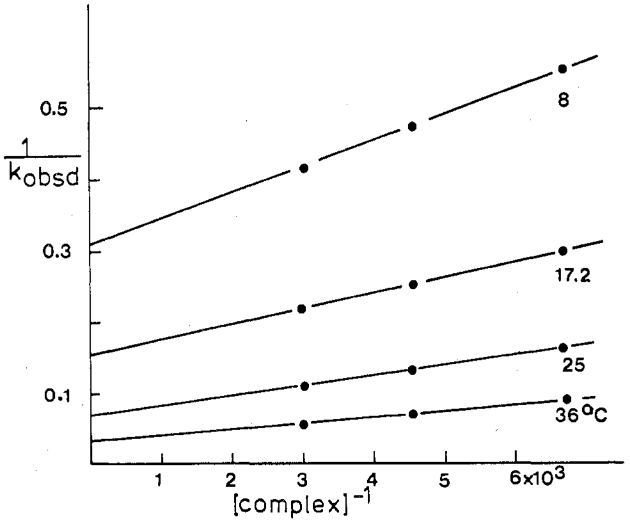


Figure 3. Plot of k_{obsd}^{-1} vs. [**2**]$^{-1}$ at different temperatures (concentration of [Ti(OH$_2$)$_6$]$^{3+}$ 0.3 × 10^{-4} M; pH 5.2, acetate buffer, μ = 0.05 M) for the decomposition of **9**.

sequence as in eq 7 and 8 leads to the same functional dependence of k_{obsd} on [complex] as in eq 5. Thus a plot of 1/k_{obsd} vs. [complex]$^{-1}$ should be linear (Figure 3). From the intercepts (=k_{et}^{-1}) and slopes (=($k_{et}K_f$)$^{-1}$) of Figure 3, k_{et} has been determined at different temperatures (Table I).

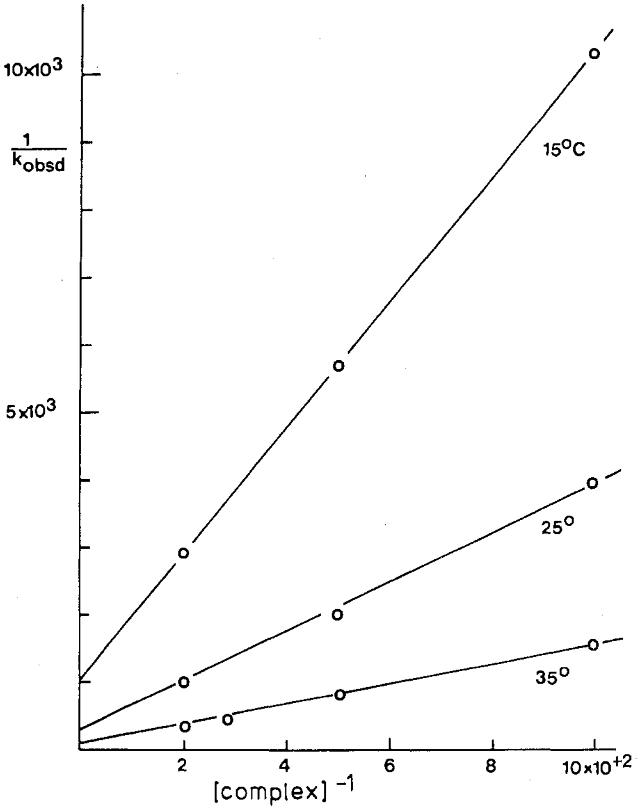


Figure 4. Plot of k_{obsd}^{-1} vs. [Co$^{III}_2$]$^{-1}$ at different temperatures for the outer-sphere reduction of the μ-[pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] complex (excess component) by [Fe(dipic)$_2$]$^{2-}$ (0.5 × 10^{-4} M) at pH 4.6 (acetate buffer, 0.01 M dipicolinic acid, μ = 0.1 M).

Table IV. Intramolecular Rate Constants and Outer-Sphere Formation Constants of the Reduction of μ-[Pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] by [Fe(dipic)$_2$]$^{2-}$ [c]

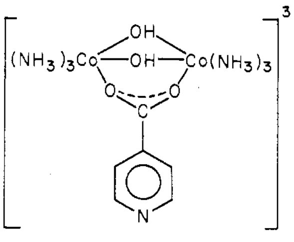
t, °C	10$^3k_{et}$, s^{-1} [a]	K_o, M^{-1} [b]
15	0.93	117
25	3.71	74
35	16.0	43

[a] Activation parameters: $\Delta H^{\ddagger}$ = 24.7 ± 0.5 kcal/mol; $\Delta S^{\ddagger}$ = +13 ± 2 cal K^{-1} mol^{-1}. [b] Thermodynamic parameters: ΔH° = −9 ± kcal/mol; ΔS° = −22 ± 6 cal K^{-1} mol^{-1}. [c] Concentration of [Fe(dipic)$_2$]$^{2-}$ 5 × 10^{-5} M; pH 4.6 (acetate buffer, μ = 0.1 M).

Reactions of μ-[Carboxylato(*O,O'*)]-dicobalt(III) Complexes with [Fe(dipic)$_2$]$^{2-}$. [Fe(H$_2$O)$_6$]$^{2+}$ reacts with excess dipicolinic acid at pH >4 forming the red 2:1 complex [Fe(dipic)$_2$]$^{2-}$. This one-electron reductant can be oxidized by cobalt(III) complexes forming Co(II) and the colorless complex [Fe(dipic)$_2$]$^-$. With binuclear cobalt(III) complexes [Fe(dipic)$_2$]$^{2-}$ reacts as follows:

$$\mathrm{Co^{III}}_2 + 2[\mathrm{Fe(dipic)_2}]^{2-} \rightarrow 2[\mathrm{Fe(dipic)_2}]^- + 2\mathrm{Co^{II}} \quad (9)$$

Reduction of the first Co(III) in μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes is the rate-determining step. Kinetic data of the reduction of the μ-[pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] cation by [Fe(dipic)$_2$]$^{2-}$ at pH 4.6–5.6 (acetate buffers, pseudo-first-order conditions with [Co$^{III}_2$] in excess over the reductant) are summarized in Table III. The dependence of k_{obsd} on [Co$^{III}_2$] is found to be less than first



order. The functional dependence conforms to eq 10, where

$$k_{obsd} = \frac{k_{et}K_o[Co^{III}_2]}{1 + K_o[Co^{III}_2]} \qquad (10)$$

K_o is the outer-sphere precursor complex (ion-pair) formation constant (eq 11) and k_{et} is the intramolecular outer-sphere rate constant (eq 12). k_{et} has been evaluated from intercepts

$$[Co^{III}_2]^{3+} + [Fe(dipic)_2]^{2-} \underset{}{\overset{K_o}{\rightleftharpoons}} \{[Co^{III}_2]^{3+}[Fe(dipic)_2]^{2-}\} \qquad (11)$$

$$\{[Co^{III}_2]^{3+}[Fe(dipic)_2]^{2-}\} \xrightarrow{k_{et}} \{[Co^{III}Co^{II}]^{2+}[Fe(dipic)_2]^{-}\} \xrightarrow{\text{rapid}} \text{products} \qquad (12)$$

($=1/k_{et}$) and K_o from slopes ($=(k_{et}K_o)^{-1}$) of straight lines of plots of k_{obsd}^{-1} vs. $[Co^{III}_2]^{-1}$ (Figure 4). Numerical values are summarized in Table IV. Activation parameters for k_{et} have been determined from an Eyring plot ($\Delta H^{\ddagger} = 24.1 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = +13 \pm 2$ cal K^{-1} mol^{-1}). The thermodynamic parameters for the outer-sphere association constant, K_o, are $\Delta H^{\circ} = -9 \pm 2$ kcal mol^{-1} and $\Delta S^{\circ} = -22 \pm 6$ cal K^{-1} mol^{-1}.

In the reduction of the corresponding μ-acetato-di-μ-hydroxo-bis[triamminecobalt(III)] complex ($(1–15) \times 10^{-3}$M) by $Fe(dipic)_2^{2-}$ (1×10^{-4} M) at 25 °C ($\mu = 0.2$ M), a simple linear dependence of k_{obsd} on $[Co^{III}_2]$ has been detected. A second-order rate constant, k_{Fe}, of $(1.27 \pm 0.10) \times 10^{-2}$ M^{-1} s^{-1} has been determined. On the assumption that $K_o[Co^{III}_2] \ll 1$ under our experimental conditions, eq 10 reduces to $k_{obsd} = k_{et}K_o[Co^{III}_2]$ which is of the observed form.

Interestingly, the corresponding μ-[pyridine-4-carboxylato]-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] complex is not reduced by $[Fe(dipic)_2]^{2-}$ under the same conditions as above. No changes of the visible absorption spectrum of solutions containing the reactants could be detected for 3 days at 25 °C.

Reactions of μ-[Carboxylato(*O,O'*)]-dicobalt(III) Complexes with $[Ti(dipic)_2]^-$. The complex anion $[Ti(dipic)_2]^-$ formed at pH 4 from dipicolinic acid and $[Ti(OH_2)_6]^{3+}$ in aqueous solution is a strong one-electron reductant. The stoichiometry of its reaction with binuclear cobalt(III) is as in eq 13.

$$[Co^{III}_2] + 2[Ti(dipic)_2]^- \rightarrow 2Co^{II} + 2[Ti^{IV}(dipic)_2] \qquad (13)$$

Reduction of the first Co(III) center is again the rate-determining step. Kinetic data of the reductions of some μ-[carboxylato(*O,O'*)]-dicobalt(III) complexes ($(0.5–7.0) \times 10^{-3}$ M) in acetate buffer solutions (pH 4.0–5.0, $\mu = 0.1$ M) by $[Ti(dipic)_2]^-$ by use of pseudo-first-order conditions (excess oxidant) are summarized in Table V. No effect on the rate of reductions was observed by added dipicolinic acid (0.001–0.01 M). The observed dependencies on the $[Ti(dipic)_2]^-$ and $[Co^{III}_2]^{3+}$ concentrations conform to the simple second-order rate law given in eq 14. Due to the reduced

$$-d[Ti(dipic)_2]/dt = k_{Ti}[Co^{III}_2][Ti(dipic)_2] \qquad (14)$$

negative charge of the $[Ti(dipic)_2]^-$ anion as compared to $[Fe(dipic)_2]^{2-}$, the outer-sphere association constant, K_o, is smaller. With the assumption of the same mechanism to be operative as in eq 11 and 12, the product $K_o[Co^{III}_2] \ll 1$, and eq 10 reduces to $k_{obsd} = k_{et}K_o[Co^{III}_2] = k_{Ti}[Co^{III}_2]$ which is of the observed form, eq 14. Measured second-order rate constants are summarized in Table VI.

Contrary to the results with $[Fe(dipic)_2]^{2-}$ being the reductant, μ-[carboxylato(*O,O'*)]-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)] complexes are reduced by $[Ti(dipic)_2]^-$ (Table VI).

Table V. Kinetic Data of the Reductions of Some Binuclear μ-Carboxylato Cobalt(III) Complexes by $[Ti(dipic)_2]^{-\,a}$

t, °C	$10^3[Co^{III}_2]$, M	10^4k_{obsd}, s^{-1}
μ-(Pyridine-4-carboxylato)-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)]		
25	1.0	0.5
	2.4	1.1
	4.7	2.6
	7.1	4.5
35.5	2.4	5.4
	4.7	9.8
46.5	2.4	17.1
	4.7	32.5
μ-(Pyridine-4-carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)]		
10.5	0.5	5.9
	1.0	12.6
	2.0	24.9
	4.0	50.1
25	0.5	21.1
	1.0	40.2
	2.0	83.0
35	0.5	52.7
	1.0	104.0
	2.0	201.0
μ-Benzoato-di-μ-hydroxo-bis[triamminecobalt(III)]		
25	0.25	4.2
	0.5	9.3
	1.0	17.1
	2.0	34.5
μ-(Pyrazinecarboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)]		
25	0.5	25.9
	1.0	54.1
	2.0	104.0
	3.0	145.0
μ-Acetato-di-μ-hydroxo-bis[triamminecobalt(III)]		
25	0.5	4.3
	1.0	9.0
	4.0	34.0
	6.0	49.1

[a] Concentration of $[Ti(dipic)_2]^-$ 5×10^{-5} M; pH 4–5 (acetate buffer), 0.01 M dipicolinic acid ($\mu = 0.1$ M).

Table VI. Summary of Second-Order Rate Constants for the Reductions of Binuclear μ-[Carboxylato(*O,O'*)] Cobalt(III) Complexes by $[Ti(dipic)_2]^{-\,b}$

complex[a]	k_{Ti}, M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}
NH_3-acetate	0.82 ± 0.02		
NH_3-benzoato	1.77 ± 0.05		
NH_3-pyridine-4-carboxylato	4.15 ± 0.1	14 ± 1	−8 ± 3
NH_3-pyrazine-carboxylato	5.17 ± 0.1		
(nane)-pyridine-4-carboxylato	0.077 ± 0.002	17.7 ± 0.8	−4 ± 2

[a] NH_3-carboxylato = μ-[carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] complexes; (nane)-pyridine-4-carboxylato = μ-[pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[1,4,7-triazacyclononanecobalt(III)]. [b] Concentration of $[Ti(dipic)_2]^-$ 5×10^{-5} M; 25 °C; pH 5.0 (acetate buffer), 0.01 M dipicolinic acid ($\mu = 0.1$ M).

Discussion

The common feature of the reactions of binuclear cobalt(III) complexes **1** and **2** with $[Fe(OH_2)_6]^{2+}$ and $[Ti(OH_2)_6]^{3+}$, respectively, is the formation of inner-sphere 1:1 precursor complexes (e.g., **6** and **7**) at pH 2–3 and 2:1 complexes at higher pH values (complexes **4**, **5**, **8**, and **9**). The redox activity of these complexes spans a large range: **5** is stable toward redox activity whereas **8** is a transient intermediate with a half-life of 22 ms at 25 °C. The structural details of the bridging moieties between the Fe(II)/Co(III) or Ti(III)/Co(III) couples are essentially identical for all these inner-sphere precursor complexes: the reducing Fe(II) or Ti(III) centers are coordinated to a tridentate pyridine-2,6-dicarboxylate, and the oxidizing Co(III) centers are bonded to a carboxylato(*O,O′*) bridge which is connected via a C–C covalent bond to the pyridine ring coordinated to the reductants in the 4 position. Oxidants and reductants are rigidly separated by ca. 9.1–9.6 Å as can be deduced from space-filling models. No direct interaction of the first coordination spheres of the reacting metal ions can occur.[24,25] The most important point of this study is the fact that the reducing power of the reductants (Fe(II) or Ti(III)) can be varied (this is achieved by the formation of 1:1 and 2:1 complexes, respectively), and, independently, the oxidizing ability of the Co(III) centers can be varied (by changing the nonbridging ligands at the cobalt(III) ions), *but the structural details between the reactants remain unchanged.*

From the data in Table I it follows clearly that for the Co(III)/Fe(II) couple both parameters—the oxidizing and reducing ability of the involved metal ions—affect the rate of intramolecular ET: the 1:1 complexes of **1** and **2** with $[Fe(OH_2)_6]^{2+}$, respectively, do not undergo thermal ET, and in the case of the respective 2:1 complexes (**4** and **5**) only **4** produces Fe(III) and Co(II).[26] Substitution of NH_3 groups at the Co(III) centers by a cyclic secondary amine reduces the oxidizing power of Co(III) substantially and decreases thereby the overall free energy change of the intramolecular reaction.

A different pattern emerges for the reactions of **1** and **2** with the strong reductant $[Ti(OH_2)_6]^{3+}$. The rate of intramolecular ET appears to be very sensitive to changes of the reducing power of the Ti(III) center. Thus the 1:1 precursor complexes **6** and **7** are much more stable ($t_{1/2}$(25 °C) ≈ 3–30 s) than the corresponding 2:1 complexes **8** and **9** ($t_{1/2}$(25 °C) ≈ 0.02–0.05 s). Contrary to the results obtained for the Fe(II) reductions, only a marginal effect on the intramolecular ET rate exists in going from precursor **6** to **7** or from **8** to **9**, respectively. A decrease of oxidizing ability of the Co(III) centers does *not* reduce the rate of intramolecular ET. This is nicely corroborated by the respective activation parameters (Table I). The enthalpies of activation are—within experimental error—identical for the 1:1 precursor complexes **6** and **7** ($\Delta H^\ddagger$ = 19 kcal/mol) and for the 2:1 complexes **8** and **9** ($\Delta H^\ddagger$ = 14.5 kcal/mol). It would appear that the observed small differences of rates are mainly due to small differences in the respective entropy of activation. The precision of the data obtained does not allow a more detailed discussion of the source of these differences, should there be any at all.

The most plausible mechanism for ET within the Ti(III)-containing inner-sphere precursor complexes would be the intramolecular formation of a transient radical intermediate:

$$[\mathrm{Co^{III}}_2\mathrm{LTi^{III}}] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{Co^{III}}_2\dot{\mathrm{L}}\mathrm{Ti^{IV}}] \xrightarrow{k_2} \text{products} \tag{15}$$

$$[\mathrm{Co^{III}}_2\mathrm{LTiLCo^{III}}_2] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\mathrm{Co^{III}}_2\dot{\mathrm{L}}\mathrm{Ti^{IV}LCo^{III}}_2] \xrightarrow{k_2} \text{products} \tag{16}$$

The limiting situation can be considered for the above mechanism: if $k_2 \gg k_{-1}$ the observed first-order rate constant $k_{\mathrm{obsd}} = k_1$, i.e., formation of the transient radical is the rate-determining step. In this instance the actual Co(III)/Co(II) reduction potential does not affect the rate of intramolecular ET—provided that the remote Co(III) centers do not change the electron-acceptor capability of the pyridine ring. Therefore, we feel that a chemical (two-step) mechanism is operative for the intramolecular reduction of Co(III) by the strong reductant Ti(III) within the structurally very similar inner-sphere precursor complexes **6**, **7** and **8**, **9**.

Intramolecular ET reactions between two metal ions can proceed without an "orbital-coupling mechanism" through the bridging ligand which in this case serves only to bring the reacting centers in close proximity.[24,25] In other words, the bridging ligand may not supply the energetically most favorable route for the ET process. It exhibits all the characteristics of an outer-sphere ET reaction. Although the distance between the redox-active metal ions of the present precursor complexes is large and rigid (in contrast to complexes studied in ref 24, 25, and 29), such an outer-sphere mechanism must be considered. It is a great advantage of our system that simple cleavage of the C–C bonds between the 4-carboxylato(*O,O′*) groups and the pyridine rings of complexes **4**, **5** and **8**, **9**, respectively, affords reactants which can react only via an outer-sphere mechanism: a binuclear cobalt(III) complex of the μ-[carboxylato(*O,O′*)]-di-μ-hydroxo-bis[amminecobalt(III)] type and $[Fe(dipic)_2]^{2-}$ or $[Ti(dipic)_2]^-$. Since both the oxidizing cobalt(III) and the reducing Fe(II) (or Ti(III)) centers retain their immediate ligand environment, the overall free energy change for the reduction reaction is not considered to be dramatically changed (the redox potentials Co(III)/Co(II) and Fe(II)/Fe(III) or Ti(III)/Ti(IV) should remain unaffected by the formal C–C cleavage). Thus it should be possible to compare two very similar ET processes which differ only by the nature of the precursor complex which is of the inner-sphere type in one instance and of the outer-sphere (ion-pair) type[29] in the other.

From the kinetic data (Table III) of the reduction of the μ-[pyridine-4-carboxylato(*O,O′*)]-di-μ-hydroxo-bis[triamminecobalt(III)] by $[Fe(dipic)_2]^{2-}$, the outer-sphere formation constant, K_o, and the first-order rate constant for the ET within this ion pair (eq 11 and 12) have been determined (Table IV). A most significant result of this investigation is the finding that the intramolecular ET rate constants, k_{et}, and the respective activation parameters for the ET processes within the precursor complex **4** (inner-sphere type) and the (3+,2−) ion pair (outer-sphere type) are identical within experimental error (Tables I and IV). Thus the existence of an uninterrupted covalent bond system as in **4** apparently does *not* provide an energetically favorable route for electron transport; we therefore assign a resonance ET within the inner-sphere precursor complex **4** across the relatively large distance of 9–9.5 Å, which exhibits very similar activation requirements as the outer-sphere process (eq 12). Note that the analogous binuclear cobalt(III) complex containing the 1,4,7-triazacyclononane ligand is redox inactive toward $[Fe(dipic)_2]^{2-}$ as is the inner-sphere precursor complex **5**.

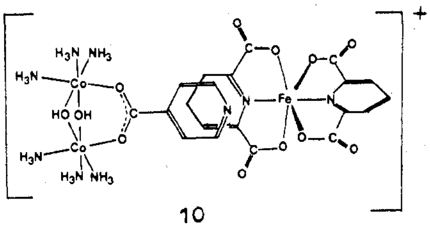
Some comments on the magnitude of the ion-pair formation constant, K_o, and the thermodynamic parameters ΔH° and ΔS° (Table IV) are in order. Equation 17, taking into

$$K_o = \frac{4\pi N a^3}{3000}\exp(-U(a)/kT) \tag{17}$$

$$U(a) = z_1 z_2 e^2/Da(1 + \kappa a) \qquad \kappa = (8\pi N e^2 \mu/1000DkT)^{1/2}$$

consideration electrostatic forces between charged species in a dielectric medium, has been successfully used to estimate at least the order of magnitude of K_o.[6,27] Definitions of the parameters are as follows: N, Avogadro's number; a, distance of closest approach; k, Boltzmann's constant; T, absolute temperature; z_1 and z_2, charges on ions 1 and 2, respectively; e, electronic charge; D, bulk dielectric constant of the solvent; μ, ionic strength.

Using the same distance of closest approach as in the inner-sphere precursor complexes of 9.0–9.5 Å, we calculate a value for $K_o \approx 22\ \mathrm{M^{-1}}$ (25 °C, μ = 0.1 M) for the μ-(pyridine-4-carboxylato)-di-μ-hydroxo-bis[triamminecobalt(III)]–$[Fe(dipic)_2]$ ion pair,[28,30] which is significantly smaller than the observed value of 74 $\mathrm{M^{-1}}$ (25 °C). The surprisingly large outer-sphere association constant appears to be a unique feature of this particular ion pair. With the same experimental conditions, the corresponding K_0 for the ion pair μ-acetato-di-μ-hydroxo-bis[triamminecobalt(III)]–$[Fe(dipic)_2]^{2-}$ has not been kinetically evaluated, indicating that $K_0 < 10\ M^{-1}$ in this case. It is therefore most likely that the presence of the pyridine rings in the reductant *and* the oxidant is responsible for a large formation constant. A highly ordered structure (**10**) with stacked aromatic rings may function as the redox-active outer-sphere precursor complex. The electrostatic model, eq 17, predicts $\Delta H° = 0$ kcal/mol and a positive value for $\Delta S°$ for reaction 11. The experimental data, in contrast, indicate a relatively strong exothermic process with a *negative* entropy (simple, favorable outer-sphere association of ions with opposite charges are thought to be governed by an entropy increase (liberation of solvent water from the second coordination sphere of the individual ions)). Our experimental negative value may be taken as further evidence that a highly ordered redox precursor complex is involved. The structural similarity of this outer-sphere complex **10** and the inner-sphere precursor complex **4** is quite obvious and may explain the identical intramolecular ET rate constants, with the assumption of a resonance ET to be operative in both reactions.



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The kinetic data in Table VI indicate a much less selective behavior for the analogous outer-sphere reductions of binuclear cobalt(III) complexes by the strong one-electron reductant $[Ti(dipic)_2]^-$. The second-order rate constants vary little within the series of binuclear *ammine*–cobalt(III) oxidants; a factor of 5 is observed in going from the μ-acetato complex to the μ-(pyrazinecarboxylato) complex. Obviously, the presence of an aromatic ring in some oxidants does not lead to a rate enhancement due to an increased outer-sphere association constant. By use of eq 17, a value of 5 M^{-1} (25 °C, $\mu = 0.1$ M, $a = 8$ Å) can be calculated for K_0, the ion-pair formation constant between μ-carboxylato-di-μ-hydroxo-bis[triamminecobalt(III)] complexes (3+) and the reductant $[Ti(dipic)_2]^-$. This is considered to represent a lower limit since no additional stabilizing factors which favor the ion-pair formation are taken into account. From the observed second-order rate constant, k_{Ti} (Table VI), and this calculated value for K_0 an *upper* limit of k_{et} for the ET process within the outer-sphere precursor complex can be estimated (~1 s^{-1} at 25 °C). The *measured* rate constant for the ET reaction within the inner-sphere precursor complex is larger by a factor of 30. Therefore, we conclude that the intramolecular ETs of the inner-sphere complexes **8** and **9** and of the outer-sphere complexes proceed by different mechanisms. This is further substantiated by the fact that—contrary to the behavior of **8** and **9**—a marked effect on the rate of reduction is observed upon substitution of the NH_3 ligands of the oxidant μ-[pyridine-4-carboxylato(*O,O'*)]-di-μ-hydroxo-bis[triamminecobalt(III)] by 1,4,7-triazacyclononane. The activation enthalpy for the latter outer-sphere reduction is higher by 3.7 kcal mol^{-1}.

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Registry No. **1**, 65651-26-5; **2**, 70268-12-1; **5**, 70268-13-2; **6**, 70268-14-3; **7**, 70268-15-4; **8**, 70268-16-5; **9**, 70268-17-6; $[Co(NH_3)_3(C_8H_3O_6N)](ClO_4)$, 70268-19-8; $[Co_3(NH_3)_9(OH)_2(C_8H_2O_6N)](ClO_4)_4$, 70268-21-2; $[Co_2(NH_3)_6(OH)_2(C_8H_4O_6N)](ClO_4)_3$, 70268-24-5; $[Co_2(C_{12}H_{30}N_6)(OH)_2(C_8H_4O_6N)](ClO_4)_3$, 70268-27-8; $[Ti(C_7H_3O_4N)(OH_2)_3]Cl$, 70268-28-9; $Cs[Ti(C_7H_3O_4N)_2]$, 70268-29-0; $Ba[Fe(C_7H_3O_4N)_2]$, 70287-33-1; $[Co_2(C_6H_{15}N_3)_2(OH)_2(C_6H_5NO_2)](ClO_4)_4$, 70268-32-5; $[Co_2(NH_3)_6(OH)_2(C_6H_4NO_2)]^{3+}$, 52375-40-3; $[Co_2(NH_3)_6(OH)_2(O\text{-}Ac)]^{3+}$, 46240-70-4; $[Co_2(C_6H_{15}N_3)_2(OH)_2(C_6H_4NO_2)]^{3+}$, 70268-33-6; $[Co_2(NH_3)_6(OH)_2(C_7H_5O_2)]^{3+}$, 52362-69-3; $[Co_2(NH_3)_6(OH)_2(C_5H_3N_2O_2)]^{3+}$, 62126-10-7; $[Co(NH_3)_3(OH_2)Cl_2]Cl$, 13820-77-4; $[Co_2(NH_3)_6(OH)_3](ClO_4)_3$, 22445-08-5; $[Co_2(C_6H_{15}N_3)_2(OH)_3](ClO_4)_3$, 70268-35-8; $TiCl_3$, 7705-07-9; $[Ti(OH_2)_6]^{3+}$, 17524-20-8; $[Fe(OH_2)_6]^{2+}$, 15365-81-8.

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