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A Long-Lived Binuclear Intermediate in a Cobalt(III)-Iron(II) Electron-Transfer Reaction[1]

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The complex $RoLH_2^{2+}$, where Ro = $Co^{III}(NH_3)_5$ and $L^{3-} = N(CH_2COO)_3^{3-}$, reacts with iron(II) by way of a binuclear intermediate $RoLFe^{2+}$ undergoing intramolecular electron transfer with specific rate $k_1 = (0.115 \pm 0.004)\ sec^{-1}$, $\Delta H^{\ddagger} = 18.7 \pm 1.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = 0 \pm 4$ cal deg^{-1} mol^{-1}, in glycine buffer at 25° and ionic strength 1.0 *M* ($NaClO_4$). Nonreducing metal ions M^{n+} (including the Co^{2+} and Fe^{3+} produced in the redox reaction) inhibit the reaction by preferentially forming $RoLM^{n+}$. Acid dissociation constants K_a of $RoLH_2^{2+}$ and stability constants $K_M = [RoLM^{n+}]/[RoL][M^{n+}]$ are as follows: $pK_{a_1} = 1.82 \pm 0.07$, $pK_{a_2} = 7.96 \pm 0.01$, $\Delta H_{a_1}° = -0.7$ kcal mol^{-1}, $\Delta H_{a_2}° = 3.0$ kcal mol^{-1}; $\log K_M = 4.4$ (Ca^{2+}), 8.53 ± 0.03 (Ni^{2+}) by titration methods; $\log K_M = 6.06 \pm 0.08$, $\Delta H_M° = +1.5 \pm 0.3$ kcal mol^{-1}, $\Delta S_M° = -23 \pm 2$ cal deg^{-1} mol^{-1} (Fe^{2+}); $\log K_M = 7.26 \pm 0.2$ (Co^{2+}), 8.54 ± 0.13 (Ni^{2+}), 7.57 ± 0.17 (Zn^{2+}), 10.60 ± 0.3 (Cu^{2+}), 11.40 ± 0.13 (Fe^{3+}), from the kinetic studies—all at 25° and ionic strength 1.0 *M* ($NaClO_4$). All the binuclear complexes are extremely inert as regards aquation to $RoOH_2^{3+}$ and $ML^{(n-3)+}$; some approximate aquation rate data are recorded. The electron-transfer process is discussed in relation to the analogous bimolecular reaction of $CH_3N(CH_2COO)_2Fe^{II}$ and $RoOOCCH_3^{2+}$.

It is generally recognized[2,3] that any homogeneous electron-transfer reaction can in principle be divided into three stages involving a precursor complex p with the original valencies unchanged and a successor complex s structurally similar to the precursor but with different oxidation states[4]

$$\underset{i}{A^{m+} + B^{n+}} \rightleftarrows \underset{p}{A^{m+}\cdot B^{n+}} \rightleftarrows \underset{s}{A^{(m-1)+}\cdot B^{(n+1)+}} \rightleftarrows \underset{f}{A^{(m-1)+} + B^{(n+1)+}} \quad (1)$$

Until recently, experimental evidence for precursor complexes was all more or less indirect. For example, Taube pointed out that a possible reason for low activation energies of many cobalt(III)-chromium(II) reactions could be that step i → p is endothermic.[5] His prediction that in some cases the overall heat of activation might be negative was verified by Endicott, *et al.*, for a number of halide-bridged cobalt(III)-chromium(II) reactions.[6] Fay and Sutin showed that the relative rates of chromium(II) reduction of $Cr^{III}NCS^{2+}$, $Cr^{III}N_3^{2+}$, and $Cr^{III}SCN^{2+}$ could be rationalized quantitatively only when the differing stabilities of precursor complexes were taken into account.[7] Liteplo and Endicott obtained kinetic evidence of cobalt(III)-chromium(II) complexes having lifetimes long enough to permit acid-base reactions as well as internal electron transfer.[8] Also there is a group of reactions for which it appears that precursor formation is the rate-limiting step[9] and in one case[10] the temperature dependence has been interpreted on the basis that at low temperatures step i → p (eq 1) is rate limiting, while at higher temperatures the complex is present in equilibrium with the starting materials and step p → s is rate limiting.

In none of these reactions is the precursor complex directly observed: in each case the most that can be deduced is that the probability of electron transfer within the complex is similar to the probability of some alternative reaction—diffusion, protolysis, ligand exchange. The lifetime of the precursor could be obtained only if its stability were known from some independent source. In theories of electron transfer[11] the stability has been calculated from simple electrostatic models, but in a few examples of inner-sphere reactions it has been possible to estimate it by analogy with other systems not involving electron transfer.[12,13] The lifetime of a typical hydroxide-bridged cobalt(III)-chromium(II) precursor, thus calculated,[12] turns out to be of the order of 10^{-6} sec; but in the case of cobalt(III)-iron(II) reactions, similar calculations lead to estimates in the range 10^{-2}-10^{+1} sec, depending on the particular complexes employed. These considerations prompted us to devise a system in which the precursor complex would be directly observable, by having step i → p thermodynamically favorable while step p → s is slow. The complex $Co^{III}(NH_3)_5OOCCH_2N(CH_2COO)_2$ proved satisfactory for this purpose and we now report studies of its reactions with iron(II) and a number of nonreducing metal ions. Shortly after preliminary communication of this work[1] Gaswick and Haim reported equally direct observations on the precursor complex of the $Co^{III}(NH_3)_5OH_2^{3+}$-$Fe^{II}(CN)_6^{4-}$ reaction[14] and more recently Hurst and Lane have reported slow electron transfer in cobalt(III)-copper(I) complexes.[15]

Experimental Section

Materials. Nitrilotriacetic acid (BDH Analytical Reagent grade) was purified repeatedly by adding mineral acid (HCl or $HClO_4$) to the solution of the disodium salt. Recrystallization of the free acid from water gave a product slightly inferior in appearance (faintly yellow), but no difference was found in the kinetic behavior of cobalt complexes prepared from either sample of the acid.

Glycine. The free acid (BDH Reagent grade) was repeatedly recrystallized from water.

Nitrilotriacetatopentaamminecobalt(III) Perchlorate.[16] Carbonatopentaamminecobalt(III) nitrate was prepared by the method of Basolo and Murmann[17] and the absence of significant amounts of tetraamminecobalt(III) in the recrystallized product was demonstrated

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[1] Preliminary report: R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, 92, 3800 (1970).

[2] N. Sutin, *Accounts Chem. Res.*, 1, 225 (1968).

[3] N. S. Hush, *Trans. Faraday Soc.*, 57, 557 (1961).

[4] Hush used the notation p and q to denote "states immediately preceding and succeeding the electron transfer" (ref 3, p 559). The convenient term "precursor complex" due to Sutin[2] will be used here.

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[8] (a) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, 91, 3982 (1969); (b) *Inorg. Chem.*, 10, 1420 (1971).

[9] H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970, p 44.

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[13] R. D. Cannon, *Nature (London)*, 228, 644 (1970).

[14] D. Gaswick and A. Haim, *J. Amer. Chem. Soc.*, 93, 7347 (1971).

[15] J. K. Hurst and R. H. Lane, *J. Amer. Chem. Soc.*, 95, 1703 (1973).

[16] Throughout this paper we use the symbols Ro for $Co^{III}(NH_3)_5$, gly^- for $H_2NCH_2COO^-$, L^{3-} for $N(CH_2COO)_3^{3-}$, and L'^{2-} for $CH_3N(CH_2COO)_2^{2-}$; $\{H^+\}$ denotes hydrogen ion activity 10^{-pH}; symbols in brackets, *e.g.*, $[H^+]$, denote concentrations.

[17] F. Basolo and R. K. Murmann, *Inorg. Syn.*, 4, 171 (1956).

by heating a sample with concentrated hydrochloric acid. (The pentaammine yields insoluble red $RoCl_3$; the tetraammines are reduced to blue $CoCl_4^{2-}$). The carbonato complex, suspended in water to form a paste, was treated with 2 equiv of concentrated perchloric acid and then with an aqueous suspension of 5 equiv of H_3L and 7.5 equiv of NaOH. After heating at 75° for 1 hr the mixture was filtered while hot to remove undissolved H_3L, cooled, and treated with 72% perchloric acid until precipitation was complete. After further cooling in ice, the mixture was filtered and the solid extracted with water at 75°. The red-orange solid obtained on cooling was repeatedly recrystallized from water (slightly acidified with $HClO_4$) at 65° until good crystals were obtained. Cobalt was determined spectrophotometrically as $CoCl_4^{2-}$, by decomposing the complex in boiling dilute alkali and making up with concentrated HCl under standard conditions. An authentic sample of $RoOH_2(ClO_4)_3$ was used as standard. Carbon, hydrogen, and nitrogen were determined by standard microanalytical methods. *Anal.* Calcd for $Co(NH_3)_5LH_2(ClO_4)_2$: C, 13.5; N, 15.8; H, 4.3; Co, 11.1; mol wt, 534. Found: C, 13.1; N, 15.8; H, 4.9; Co, 11.6; mol wt by pH titration, 538.

Absorption spectra are shown in Figure 1.

Potentiometric titration in aqueous solution,[18] ionic strength 1.0 *M* ($NaClO_4$), yielded $pK_{a1} = 1.82 \pm 0.07$ and $pK_{a2} = 7.96 \pm 0.01$ at 25° and $pK_{a1} = 1.74 \pm 0.20$ and $pK_{a2} = 8.30 \pm 0.02$ at 6° (eq 2a, 2b below). Hence $\Delta H_{a1} = -0.7$ kcal mol^{-1} and $\Delta H_{a2} = 3.0$ kcal mol^{-1}. These may be compared with corresponding data for *N*-methyliminodiacetic acid under the same conditions,[19] namely, $pK_{a1} = 2.20$ and $pK_{a2} = 9.27$ at 25° and $\Delta H_{a1} = 0.0$ and $\Delta H_{a2} = 6.6$ kcal mol^{-1}; for nitrilotriacetic acid at 20°, $pK_{a1} = 1.99$, $pK_{a2} = 2.27$, and $pK_{a3} = 8.96$.[20] There was no evidence of the triprotonated species $RoLH_3^{3+}$ and we tentatively assign the dissociation constant $K_{a3} = [RoLH_2^{2+}] \cdot \{H^+\}/[RoLH_3^{3+}]$ a limit of $pK_{a3} \lessdot 0.2$.[16]

Iron(II) was prepared in solution by dissolving 99.99% pure iron sponge (Koch-Light Laboratories Inc.) in a slight excess of perchloric acid, previously deaerated by bubbling nitrogen scrubbed by passage through chromium(II) solution, and stored in an all-glass apparatus. Ferrous content was determined by permanganate titration and excess acid by potentiometric titration with NaOH in an atmosphere of nitrogen or alternatively by injecting aliquots into a glycine buffer, also under nitrogen, and comparing the pH drop with that produced by perchloric acid at the same ionic strength. In some series of experiments (see Tables III and IV below) ferrous ammonium sulfate (BDH Analytical grade) was used.

Perchloric acid used in all experiments was the Analytical grade, 72% $HClO_4$. Sodium perchlorate solutions were obtained by neutralizing this with "AnalaR" sodium hydroxide. Metal perchlorates other than ferrous were supplied by G. F. Smith Co. Other materials were of Analytical Reagent grade.

Equilibrium Measurements. Acid dissociation constants for $RoLH_2$ and stability constants of metal complexes were determined by potentiometric titration,[18] using the EIL "Vibret" expanded-scale pH meter with glass and calomel electrodes. The salt bridge for the calomel electrode contained saturated NaCl instead of KCl, since otherwise it tended to become clogged with $KClO_4$. The system was standardized at pH 1.10, 4.0, and 9.0 using 0.10 *M* HCl[21] and the usual potassium phthalate and borax buffers, respectively. The system was found to be self-consistent within the limits of reproducibility, *i.e.*, within ±0.005 unit of pH.

Kinetic Measurements. Reactions were carried out under an atmosphere of nitrogen, scrubbed by passage through 0.1 *M* chromium(II) solutions continuously regenerated by means of amalgamated zinc (Analytical Reagent grade). Reactions were followed spectrophotometrically in an instrument fitted with an automatic cell changer. Four cells were placed in the light beam in rotation at fixed time intervals, so that up to three kinetic runs could be carried out simultaneously, the fourth cell being used for the blank readings. Faster reactions were carried out singly on a Beckman DB spectrophotometer with a 10-in. chart recorder.

Glycine-perchloric acid buffers were used over the pH range 1.9-3.3, and dilute perchloric acid was used when lower pH was required. Ionic strength was maintained by means of sodium perchlorate. Solutions were deoxygenated for at least 10 min in the cell compartment of the spectrophotometer. When the temperature was steady within ±0.1°, ferrous solution at the same temperature was injected from a Hamilton 1000-μl syringe fitted with a Cheney adaptor. The rate of disappearance of Co(III) was followed by means of the decrease in absorbance at 502 nm. It was established in separate experiments that at this wavelength the absorbances of Fe^{III} and Co^{II}, both in glycine buffer and in aqueous perchloric acid, are comparatively small.

Results

I. Observations on Binuclear Complexes $RoLM^{n+}$. Solutions of nitrilotriacetatopentaamminecobalt(III) vary in color with changing pH (Figure 1). In all three complexes $RoLH_2^{2+}$, $RoLH^+$, and RoL, the lowest d-d transition is at 502 nm, ϵ 70 M^{-1} cm^{-1}, similar to that for the acetatopentaammine complex (503 nm).[22] The band at 351 nm (ϵ 56 M^{-1} cm^{-1}) changes very little on going from $RoLH_2^{2+}$ to $RoLH^+$, but removal of the second proton produces a slight shift to violet and a large increase in intensity changing the color from pink to orange. Presumably this is due to the tertiary amino and carboxyl groups moving into the second coordination sphere of the cobalt (compare the similar changes associated with ion pair formation, *e.g.*, between $RoOH_2^{3+}$ and SO_4^{2-}).[23]

On the addition of calcium ion the orange solution changes instantly to pink and the spectrum reverts toward that of $RoLH^+$. There is no sign of total decomposition of the complex: the spectrum remains constant with time, the band at 502 nm remains unaffected, and the spectrum is quite different from that of an equivalent mixture of $RoOH_2^{3+}$ and CaL^{2-} (Figure 1). Exactly parallel observations were made with Ni^{2+} and Fe^{3+} in place of Ca^{2+} ion, except that in the latter case the band at 351 nm was obscured by the intense Fe^{III} spectrum.

Potentiometric titrations of equimolar mixtures of $RoLH_2^{2+}$ and Ca^{2+} or Ni^{2+} with alkali yielded the characteristic complex formation curves and on back-titration with acid the same curves were retraced within the limits of reproducibility of the pH meter. The usual calculations[18] yielded consistent stability constants for the formation of 1:1 complexes (eq 3, $M^{n+} = Ca^{2+}, Ni^{2+}$), as shown in Table I.[19,24] The stability constant of the complex of Ni^{2+} with *N*-methyliminodiacetic acid was determined in the same way for comparison (Table I).

$$RoLH_2^{+} \xrightleftharpoons{K_{a1}} RoLH^+ + H^+ \tag{2a}$$

$$RoLH^+ \xrightleftharpoons{K_{a2}} RoL + H^+ \tag{2b}$$

$$RoL + M^{n+} \xrightleftharpoons{K_M} RoLM^{n+} \tag{3}$$

II. Aquation of the RoL Group. In strongly acid solution the complex $RoLH_2^{2+}$ slowly decomposes according to

$$RoLH_2^{2+} + H^+ \rightarrow RoOH_2^{3+} + H_3L \tag{4}$$

Spectrophotometric measurements at 255 nm in the range $[H^+] = 0.04\text{-}0.40\,M$ yielded a two-term rate law

$$-d[RoLH_2^{2+}]/dt = (k + k'[H^+])[RoLH_2^{2+}] \tag{5}$$

with $k = (2.1 \pm 0.1) \times 10^{-5}$ sec^{-1} and $k' = (1.8 \pm 0.4) \times 10^{-5}$ M^{-1} sec^{-1} at 79°, ionic strength 1.0 *M* ($NaClO_4$-$HClO_4$). (Compare the corresponding aquation of $RoOOC{\cdot}CH_2NH_3^{3+}$: $k = 0.28 \times 10^{-5}$ sec^{-1}, $k' = 4.2 \times 10^{-5}$ M^{-1} sec^{-1}).[25]

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Table I. Stability Constants of $RoLM^{n+}$ and Related Complexes

	$\log K_M(RoL + M^{n+} \rightleftharpoons RoLM^{n+})^a$		$\log K(M^{n+} + L^{x-} \rightleftharpoons ML^{(n-x)+})^c$				
			$H_2NCH_2COO^-$		$CH_3N(CH_2COO)_2{}^{2-}$		$N(CH_2COO)_3{}^{3-}$
M^{n+}	Kinetic method	Titration method	20°, I = 0.1 M	25°, I = 1.0 M	20°, I = 0.1 M	25°, I = 1.0 M	20°, I = 0.1 M
Ca^{2+}		4.4 ± 0.1	2.59		3.75		6.41
Fe^{2+}	6.05 ± 0.08[b]			3.83	6.65	5.99[d]	8.83
Co^{2+}	7.26 ± 0.17		4.7[e]		7.62		10.6
Ni^{2+}	8.51 ± 0.13	8.53 ± 0.03	5.73	5.70	8.73	8.51[f]	11.26
Cu^{2+}	10.6 ± 0.3		8.12	8.33	10.09		12.68
Zn^{2+}	7.57 ± 0.17		5.16		7.66		10.45
Fe^{3+}	11.40 ± 0.13			10.0			15.87
H^+		7.96 ± 0.01	9.85	9.65	9.65	9.27[d]	9.73

[a] Temperature 25°; ionic strength 1.0 M ($NaClO_4$). [b] Also $\Delta H_{Fe(II)} = 1.5 \pm 0.3$ kcal mol^{-1} and $\Delta S_{Fe(II)} = 23 \pm 2$ cal deg^{-1} mol^{-1}. [c] From ref 24, except as otherwise stated. [d] Reference 19. [e] Ionic strength 0.15 M. [f] This work.

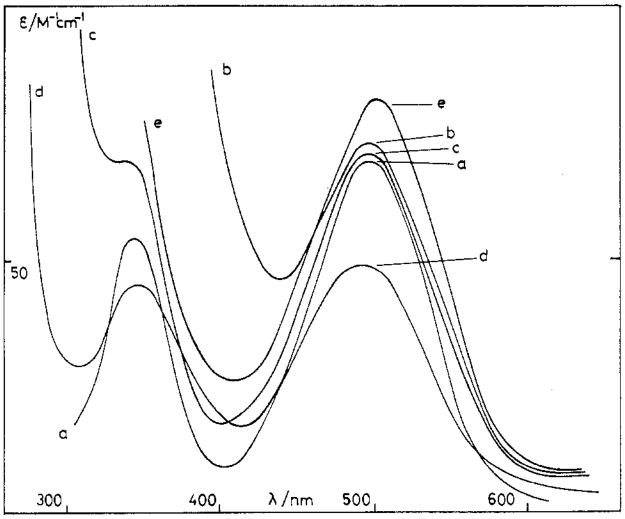

Figure 1. Absorption spectra of nitrilotriacetatopentaammine-cobalt(III) species in aqueous solution: (a) $RoLH_2{}^+$ ($HClO_4$, pH 2); (b) RoL (NaOH, pH 11); (c) $RoLCa^{2+}$, in presence of slight excess of Ca^{2+} (pH ~7); (d) $RoOH_2{}^{3+}$ and CaL^{2-} in equivalent amounts (pH ~7); (e) $RoLFe^{2+}$ in glycine buffer (pH 3.3, 0°).

Aquation of the binuclear complexes with metal ions (eq 6) was studied in glycine buffer or perchloric acid as appropriate, such that at least 90% of the cobalt(III) initially present was in the form $RoLM^{n+}$. Because of the very slow rates of reaction, rate constants were calculated from the initial rates of change in absorbance (at 255 nm) and "final" values measured on equivalent solutions of $RoOH_2{}^{3+}$, M^{n+}, and H_3L. Rates were independent of the presence of excess M^{n+} ion and varied little from one metal M to another (Table II). The effect of acid concentration could be studied only with the most stable complex, $RoLCu^{2+}$: no significant change in rate resulted from a 25-fold change in $[H^+]$. The positions of equilibrium in the reactions 6 were not determined but it was noted that in glycine buffer, mixtures of $RoOH_2{}^{3+}$, Ni^{2+}, and H_3L underwent slow spectral changes consistent with formation of $RoLNi^{2+}$, while a mixture of $RoOH_2{}^{3+}$ and $Fe^{III}L$ at $[H^+]$ = 31.8 mM completely failed to react.

$$RoLM^{n+} \xrightarrow{k''} RoOH_2{}^{3+} + ML^{(n-3)+} \tag{6}$$

III. Kinetics of Electron Transfer. A. Treatment of Kinetic Data. In all experiments, iron(II) was taken in large excess over cobalt(III), so that *pseudo*-first-order kinetics might be expected, and rate constants k_{obsd} would be obtained from the usual semilogarithmic plots based on eq 8. $[Co^{III}]_T$ is the total stoichiometric concentration of cobalt(III) species and A_0, A, and A_∞ are absorbances at times 0, t, and infinity, respectively. In practice, many experiments showed appreciable deviation toward slower rates as reaction proceeded and a more elaborate analysis was required. Of various methods considered the following was selected as being the least likely to impose any prior assumptions. Values of A were read at suitable intervals and values of $-\Delta A/\Delta t$ were taken to represent $-dA/dt$. Defining "extent of reaction" x by the expression

$$-d[Co^{III}]_T/dt = k_{obsd}[Co^{III}]_T \tag{7}$$

Table II. Aquation of Binuclear Complexes:[a] $RoLM^{n+} \rightarrow RoOH_2{}^{3+} + ML^{(3-n)-}$; $k'' = -[RoLM^{n+}]^{-1} \cdot (d[RoLM^{n+}]/dt)$

M^{n+}	$10^3[M^{n+}]$, M	$10^3\{H^+\}$, M	$10^5k''$ sec^{-1}
Zn^{2+}	26.6	0.60	4.3
	287	0.60	3.7
Co^{2+}	17.3	0.60	4.1
	240	0.60	3.9
	287	0.60	3.9
Cu^{2+}	33.3	0.80[b]	4
	33.3	4.0[b]	5.4
	33.3	20.0[b]	4.8
Fe^{3+}	3.0	31.8[b]	0.05[c]

[a] At 79°; perchlorate media, ionic strength 1.0 M (Na^+), total $[Co(III)] = 3.0 \times 10^{-3}$ M. [b] Stoichiometric concentration, $[H^+]$. [c] At 25°.

$$\ln\left(\frac{A - A_\infty}{A_0 - A_\infty}\right) = -k_{obsd}t \tag{8}$$

$$x = \frac{A_0 - A}{A_0 - A_\infty} \tag{9}$$

we then have

$$k_{obsd} = \frac{-1}{[Co^{III}]_T}\frac{d}{dt}[Co^{III}]_T = \frac{1}{1-x}\frac{dx}{dt} = \frac{-1}{A - A_\infty}\frac{dA}{dt} \tag{10}$$

Plots of k_{obsd} *vs.* x usually appeared straight and could be represented by

$$k_{obsd} = k^0{}_{obsd}(1 - \alpha x) \tag{11}$$

where $k^0{}_{obsd}$ is the initial specific rate and α is a coefficient which would vary from zero for pure first-order kinetics to unity for pure second-order. In addition however, and more especially with high values of α, downward curvature could be seen as x approached 1.0. Rate constants tabulated in this paper as $k^0{}_{\mathrm{obsd}}$ were obtained by least-squares fitting of the $k_{\mathrm{obsd}}(x)$ data to eq 11, over the range $0 < x \leqslant 0.9$; those tabulated as k_{obsd} were obtained from the initial slopes of the plots corresponding to eq 8.

B. The Cobalt(III)-Iron(II) Reaction. These experiments were carried out in glycine buffer media in the pH range 1.3-3.3 (Tables III, IV). Under these conditions published stability data[24] show that the end products are free Co^{2+} ion and the chelate $Fe^{III}L$ complex; hence the overall stoichiometry is[16]

$$\mathrm{Co(NH_3)_5LH_n{}^{n+} + Fe^{2+} + (5-\mathit{n})H_2gly^+ \rightarrow Co^{2+} + 5NH_4{}^+ + Fe^{III}L + (5-\mathit{n})Hgly} \tag{12}$$

where n varies from 1 to 2. That is to say, complexation of Fe^{2+} or Co^{2+} by glycine and various possible redistributions of the L^{3-} ligand leaving the iron(III) as $Fe(gly)^{2+}$ are all negligible.[26] Certain equilibria involving the unchanged $RoLH_2{}^{2+}$ species as a ligand are however possible as will be discussed below.

The iron(II) dependence is first order at pH 2.26 (Table III) but strongly curved toward zero order at higher pH (Table IV). The hydrogen ion dependence at constant iron(II) concentration (Table IV) is complex, a plot of log $k^0{}_{\mathrm{obsd}}$ *vs.* pH varying in slope from greater than 1 below pH 2 to less than 1 above pH 3. Curvature at the acid end of the pH range is evidently associated with equilibrium 2a. A plot of log $\{k^0{}_{\mathrm{obsd}}(1 + \{H^+\}/K_{a1})[Fe^{II}]_T{}^{-1}\}$ against pH is satisfactorily straight up to about pH 2.2, but there remains a significant deviation toward lower rates at the upper end of the pH range (Figure 2). There is no dependence on glycine concentration, over a fourfold range of variation (Table IV). All these features can be summarized in a rate law involving a binuclear complex $RoLFe^{2+}$ which at high ferrous concentration or low acidity becomes the predominant cobalt(III) species

$$\mathrm{RoL + Fe^{2+} \xrightleftharpoons{K_{Fe(II)}} RoLFe^{2+}} \tag{13}$$

$$\mathrm{RoLFe^{2+} \xrightarrow{k_1} Co^{II} + Fe^{III}L} \tag{14}$$

$$\text{rate} = k_1[\mathrm{RoLFe^{2+}}] \tag{15}$$

$$= k_1 K_{\mathrm{Fe(II)}}[\mathrm{RoL}][\mathrm{Fe^{2+}}] \tag{16}$$

i.e.

$$k^0{}_{\mathrm{obsd}} = k_1 K'_{\mathrm{Fe(II)}}[\mathrm{Fe^{II}}]_T/(1 + K'_{\mathrm{Fe(II)}}[\mathrm{Fe^{II}}]_T) \tag{17}$$

where $[Fe^{II}]_T$ denotes total iron(II) concentration (assumed constant throughout a run) and

$$K'_{\mathrm{Fe(II)}} = K_{\mathrm{Fe(II)}}/(1 + \{H^+\}K_{a2}{}^{-1} + \{H^+\}^2 K_{a1}{}^{-1}K_{a2}{}^{-1}) \tag{18}$$

Plots of $(k^0{}_{\mathrm{obsd}})^{-1}$ against $[Fe^{II}]_T{}^{-1}$ yield k_1 and $K'_{\mathrm{Fe(II)}}$ as shown in Table V; these combined with the previous titration data give $K_{\mathrm{Fe(II)}}$ and the corresponding thermodynamic parameters as shown in Table I.

C. Inhibition of the Redox Reaction by Nonreducing Metals. The above rate law requires that the addition of any nonreducing metal ion M^{n+} should slow the reaction by lowering the $RoLFe^{2+}$ concentration according to the

Table III. Reactions in Glycine Buffer Mixtures[a]

pH	$10^3 \times [L]_F$, M	$10^3[M^{n+}]$, M	$10^3 \times [Fe^{II}]_T$, M	$10^3 \times k^0{}_{\mathrm{obsd}}$, sec^{-1}	$10^2 k^0{}_{\mathrm{obsd}}/[Fe^{II}]_T$, M^{-1} sec^{-1}
2.26	0.15		29.2	4.30	14.7
2.26	0.19		35.0	5.61	16.0
2.26	0.25		46.8	7.00	15.0
2.26	0.37		70.1	9.33	13.3
2.26	0.44		81.8	11.3	13.8
2.26	0.49		93.4	9.9	10.6
2.26	0.60		110.9	13.1	11.8
2.26	0.60		116.8	13.2	11.3
					Mean 13 ± 2
3.39	0.40	38.8 (Ni^{2+})	32.0^{b}	0.51	1.59
3.39	0.40	38.8 (Ni^{2+})	35.6^{b}	0.52	1.46
3.39	0.40	38.8 (Ni^{2+})	44.8^{b}	0.69	1.54
3.39	0.40	38.8 (Ni^{2+})	64.0^{b}	0.97	1.52
3.39	0.40	38.8 (Ni^{2+})	71.2^{b}	1.02	1.43
					Mean 1.4 ± 0.1
2.90	0.40	33.3 (Co^{2+})	40.8	6.91	16.9
2.90	0.40	33.3 (Co^{2+})	80.1	13.6	17.0

[a] At 25°; total [glycine] = 0.50 M; ionic strength 1.0 M ($NaClO_4$); initial [Co(III)] = 3.0×10^{-3} M. $[L]_F$ is the concentration of added free nitrilotriacetic acid. [b] Solutions contain $[NH_4{}^+] = [SO_4{}^{2-}] = 2[Fe^{2+}]_T$; total [glycine] = 1.00 M; ionic strength 1.2 M ($NaClO_4$).

Table IV. Reactions in Glycine Buffer Mixtures[a]

$[gly]_T$, M	pH	$10^3 \times [L]_F$, M	$10^3 \times [Fe^{II}]_T$, M	$10^3 k^0{}_{\mathrm{obsd}}$, sec^{-1} Obsd	$10^3 k^0{}_{\mathrm{obsd}}$, sec^{-1} Calcd[b]
Temperature 25°					
0.50	3.245	3.0	27.7	45.9	42.0
0.50	3.245	3.0	33.2	48.4	47.6
0.50	3.245	3.0	66.4	70.3^{c}	67.5
0.50	3.245	3.0	88.5	76.9	75.1
0.50	3.245	3.0	99.6	76.2	78.2
0.50	3.245	3.0	110.6	82.3	80.8
0.50	3.245		27.7	42.5	42.0
0.50	3.245		33.2	46.3	47.6
0.50	3.245		66.4	67.9	67.5
0.50	3.245		99.6	71.8	75.1
0.50	3.245		110.6	81.8	80.8
Temperature 6°					
0.50	3.30	3.0	27.7	3.16	3.08
0.50	3.30	3.0	33.2	3.60	3.59
0.50	3.30	3.0	66.4	5.87	5.57
0.50	3.30	3.0	99.6	6.64^{c}	6.86
0.50	3.30	3.0	110.6	6.92	7.18
1.00	1.25		29.1^{d}	0.14	
1.00	1.35		29.1^{d}	0.19	
1.00	1.595		29.1^{d}	0.39	
1.00	1.73		29.1^{d}	0.77	
1.00	2.04		29.1^{d}	1.90	
1.00	1.25	0.30	53.4^{d}	0.27	
1.00	1.455	0.30	53.4^{d}	0.63	
1.00	1.565	0.30	53.4^{d}	0.74	
1.00	1.73	0.30	53.4^{d}	1.51	
1.00	2.04	0.30	53.4^{d}	4.13	
1.00	2.26	0.30	53.4^{d}	6.6	
1.00	2.26	0.30	53.4^{d}	6.7	
1.00	2.47	0.30	53.4^{d}	10.4	
1.00	2.555	0.30	53.4^{d}	12.3	
1.00	2.985	0.30	53.4^{d}	28.2	
1.00	3.39	0.30	53.4^{d}	46.9	
1.00	2.26		53.4^{d}	5.7	
0.75	2.26		53.4^{d}	5.6	
0.50	2.26		53.4^{d}	4.8	
0.25	2.26		53.4^{d}	5.8	

[a] Ionic strength 1.0 M ($NaClO_4$); initial [Co(III)] = 3.0×10^{-3} M. $[gly]_T$ is the total glycine concentration; $[L]_F$ is the concentration of added free nitrilotriacetic acid. [b] Calculated from eq 17 using the parameters shown in Table V. [c] Average of two experiments. [d] Solutions contain $[NH_4{}^+] = [SO_4{}^{2-}] = 2[Fe^{2+}]_T$, ionic strength 1.2 M ($NaClO_4$).

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(26) Other iron(III) products such as $FeLOH^-$, $FeL(OH)_2{}^{2-}$, $FeOH^{2+}$, or $Fe_2(OH)_2{}^{4+}$ are also calculated[24] to be negligible; the mixed complex[16] $FeLgly^-$ might occur but its formation constant is not known.

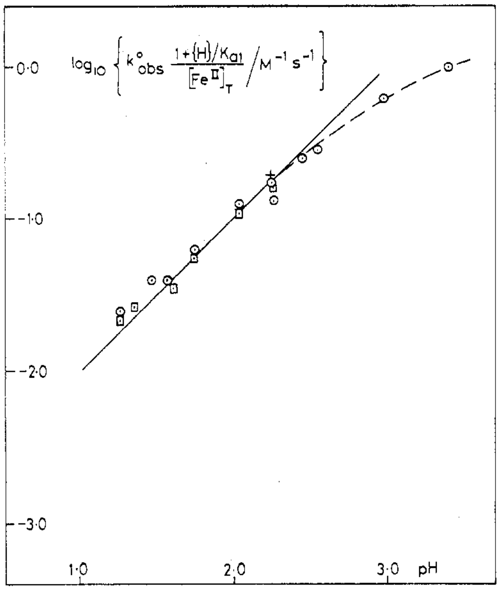

Figure 2. Hydrogen ion dependence of reaction $RoLH_n{}^{n+} + Fe^{2+}$ in glycine buffer: ⊙, $[Fe^{II}]_T = 53.4$ m*M*; ⊡, $[Fe^{II}]_T = 29.1$ m*M* (Table IV); +, $[Fe^{II}]_T = 29.1$ m*M*, interpolated from data of Table III. The straight line is drawn with unit slope.

Table V. Summary of Rate and Equilibrium Data for the $RoLH_n{}^{n+} + Fe^{2+}$ System[a]

Temp, °C	pH	$K'_{Fe(II)}$, M^{-1}	10^2k_1, sec^{-1}	$\Delta H_1{}^{\ddagger}$, kcal mol^{-1}	$\Delta S_1{}^{\ddagger}$, cal deg^{-1} mol^{-1}
6.0	3.30	12 ± 2	1.26 ± 0.05	18.7 ± 1.3	0 ± 4
25.0	3.25	21.3 ± 2	11.5 ± 0.4		

[a] $[gly]_T = 0.50$ *M*; ionic strength 1.0 *M* ($NaClO_4$).

competing equilibrium, eq 3. In agreement with this it is found that Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+} inhibit the reaction, the effect diminishing in that order, while Mn^{2+}, Ca^{2+}, and Al^{3+} have no appreciable effect. From eq 2, 3, 13, and 15 the general expression for the specific rate of the inhibited reaction is

$$k^0_{obsd} = \frac{k_1K_{Fe(II)}[Fe^{II}]_T}{1 + K_{Fe(II)}[Fe^{II}]_T + \{H^+\}/K_{a2} + \{H^+\}^2/K_{a1}K_{a2} + K_M[M^{n+}]_T} \qquad (19)$$

which may be written

$$\frac{1}{k^0_{obsd}} = \frac{1}{k_1} + \frac{1}{k_1K'_{Fe(II)}[Fe^{II}]_T} + \frac{K_M[M^{n+}]_T}{k_1K_{Fe(II)}[Fe^{II}]_T} \qquad (20)$$

where $[M^{n+}]_T$ is the concentration of added M^{n+} ion and $K'_{Fe(II)}$ is as defined above, or

$$\frac{1}{k^0_{obsd}} = \frac{1}{k^{00}_{obsd}} + \frac{K_M[M^{n+}]_T}{k_1K_{Fe(II)}[Fe^{II}]_T} \qquad (21)$$

where k^{00}_{obsd} is the specific rate observed under the same conditions in the absence of the inhibiting ion.

Cobalt(II), Nickel(II), and Zinc(II). These were studied in the same glycine buffer media as the uninhibited reaction. Neither Fe^{2+} nor the other three metals are appreciably complexed by glycine under these conditions.[24] All these reactions deviated somewhat from *pseudo*-first-order kinetics and k^0_{obsd} was calculated as described above. For the nickel and cobalt systems it was confirmed that k^0_{obsd} is a linear function of $[Fe^{2+}]_T$ (Table III) and for all three at constant $\{H^+\}$, $(k^0_{obsd})^{-1}$ is a linear function of $[M^{n+}]_T$ (Table VI). Using the values of k_1 and $K_{Fe(II)}$ obtained previously these data yield K_{Ni}, K_{Co}, and K_{Zn} as shown in Table I.

Table VI. Reactions in Glycine Buffer Mixtures in the Presence of Added Nonreducing Metal ions (M^{n+})[a]

M^{n+}	$10^3\times$ $[L]_F$, *M*	$10^3\times$ $[Fe^{II}]_T$, *M*	$10^3\times$ $[M^{n+}]_T$, *M*	$10^3\times$ k^0_{obsd},[b] sec^{-1}	$10^{-2}K_M/k_1K_{Fe(II)}$,[d] sec
None		80.2		45	
Ni^{2+}		79.8	20.0	1.50	25.7
		79.8	26.7	1.20	24.3
		79.8	33.3	0.87	27.0
		79.8	53.3	0.63	23.8
		79.8	66.6	0.50	23.7
					Mean 24.9 ± 1.3
Co^{2+}		80.1	20.0	17.4	1.40
		80.1	26.7	15.1	1.32
		80.1	33.3	12.6[c]	1.37
		80.1	53.2	8.67	1.40
		80.1	66.6	6.33	1.63
					Mean 1.42 ± 0.11
Zn^{2+}	1.50	80.2	20.0	11.4	2.65
	1.50	80.2	33.3	6.9	2.96
		80.2	33.3	7.0	2.92
	1.50	80.2	66.7	3.45	3.21
					Mean 2.9 ± 0.2

[a] At 25°, pH 2.90; $[gly]_T = 0.5$ *M*; ionic strength 1.0 *M* ($NaClO_4$); initial $[Co(III)] = 3.0 \times 10^{-3}$ *M*. $[L]_F$ is the concentration of added free nitrilotriacetic acid. [b] Obtained by fitting rate data to eq 11, within the range $0.9 > x > 0.1$. [c] Mean of five experiments. [d] Calculated as $K_M/k_1K_{Fe(II)} = (1/k^0_{obsd} - 1/k^{00}_{obsd})[Fe^{II}]_0/[M^{n+}]_T$, where $k^{00}_{obsd} = 45 \times 10^{-3}$ sec^{-1}.

Iron(III) and Copper(II). Formation of $RoLFe^{3+}$ and $RoLCu^{2+}$ appeared to be virtually complete even in dilute perchloric acid media. Reactions were too slow to follow to completion and rate constants were determined from the initial rate and a simulated infinite-time reading, measured on a made-up mixture of the products. Rates were inversely first order in $[M^{n+}]$ and independent of $[H^+]$ (Table VII) as required if the first two terms of eq 20 are negligible compared with the third

$$RoLH_2{}^{2+} + M^{n+} \rightleftharpoons RoLM^{n+} + 2H^+ \qquad (22)$$

$$RoLM^{n+} + Fe^{2+} \xrightleftharpoons{K_{Fe(II)}/K_M} RoLFe^{2+} + M^{n+} \qquad (23)$$

$$RoLFe^{2+} \xrightarrow{k_1} \text{products} \qquad (24)$$

$$k_{obsd} = \frac{k_1K_{Fe(II)}}{K_M}\frac{[Fe^{2+}]}{[M^{n+}]} \qquad (25)$$

Experiments in glycine buffer were complicated by formation of M^{n+}-gly complexes, as evidenced by intense coloration even in the absence of $RoLH_2{}^{2+}$ or H_2L^-. From data of Perrin[27] we know that Fe^{3+} is largely complexed as[16] $Fe(gly)^{2+}$ under these conditions. It was confirmed that in these systems too $(k^0_{obsd})^{-1}$ is a linear function of $[Fe^{III}]_T$, which would suggest an equilibrium of the type

$$RoLFe^{3+} + Hgly^- + Fe^{2+} \rightleftharpoons RoLFe^{2+} + Fe(gly)^{2+} + H^+ \qquad (26)$$

followed by electron transfer as before. However, the rate is also nearly independent of pH which is difficult to account for. One possibility is that the iron in $RoLFe^{3+}$ becomes

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[27] D. D. Perrin, *J. Chem. Soc.*, 3120 (1958).

Table VII. Reactions in Perchloric Acid Medium in the Presence of Added Metal ions M^{n+} [a]

M^{n+}	$10^3\times$ $[Co^{III}]_0$, M	$10^3[H^+]$, M	$10^3\times$ $[M^{n+}]_T$, M	$10^3\times$ $[Fe^{II}]_T$, M	$10^6\times$ k_{obsd}, sec^{-1}	$10^{-6}[Fe^{II}]_T/$ $k_{obsd}[M^{n+}]_T$, sec
Fe^{3+}	2.4	36.6	13.3	80.2	3.0	2.01
	2.4	36.6	6.67	80.2	6.3	1.91
	1.5	34.8	3.33	80.2	11.8	2.04
	3.0	37.8	3.33	80.2	13.4	1.80
	3.0	57.8	6.67	80.2	6.0	2.00
						Mean 1.95 ± 0.09
Cu^{2+}	3.0	27.8	33.3	80.2	8.0	0.30
	1.0	33.8	33.3	80.2	9.6	0.25
	1.92	35.6	33.3	80.2	8.3	0.29
	3.0	37.8	33.3	80.2	7.85	0.31[b]
	3.0	47.8	33.3	80.2	8.3	0.29
	3.0	37.8	66.6	80.2	7.9	0.15
	3.0	37.8	53.2	80.2	5.0	0.48
	3.0	37.8	26.7	80.2	9.4	0.32
	3.0	37.8	20.0	80.2	12.3	0.33
	3.0	37.8	13.3	80.2	19.6	0.31
						Mean 0.30 ± 0.07

[a] At 25°; ionic strength 1.0 M ($NaClO_4$). $[Co^{III}]_0$ is the initial cobalt(III) concentration. [b] Average of two experiments.

coordinated with glycine, so that the relevant equilibrium no longer involves hydrogen ion

$$RoLFe^{III}gly^{2+} + Fe^{2+} \rightleftarrows RoLFe^{2+} + Fe(gly)^{2+} \qquad (27)$$

We have not investigated the matter any further, and the value of $K_{Fe(III)}$ in Table I is derived from the experiments in perchloric acid medium. With copper(II), reactions in glycine buffer were much more rapid than those in perchloric acid but when the concentration of uncomplexed Cu^{2+} was calculated using published[24b] stability data for $Cu(gly)^+$ and $Cu(gly)_2$, the kinetic data agreed with eq 25 confirming that glycine takes no direct part in the reaction.

D. Deviation from *Pseudo*-First-Order Kinetics. The deviations referred to above can be summarized as follows. In the absence of any added metal ion and in the absence of any added chelating agent, the specific rate k_{obsd} falls by some 60% in the course of the reaction (Figure 3, curve b). The addition of cobalt(II) in amounts comparable with the initial cobalt(III) concentration lowers the rate, and has a greater effect on the initial specific rate than on the final specific rate (Table VIII; Figure 3, curve c). The inclusion of free nitrilotriacetic acid in the reaction mixture greatly reduces the effect (Table VIII; Figure 3, curve a) to the point where, with nitrilotriacetic acid in slight excess over initial cobalt(III), semilogarithmic plots (from eq 8) become straight on visual inspection. The effect becomes less pronounced at lower pH and below pH 2.3 all reactions are effectively first order. Thus far the observations are consistent with inhibition of the main reaction by the cobalt(II) product as discussed above (eq 3, $M^{n+} = Co^{2+}$). In addition, however, deviations occur in the presence of a large excess of nonreducing ion, including cobalt(II) itself. Consideration of available stability data reveals a second possible inhibition effect involving $Fe^{III}L$ jointly with the added inhibitor M^{n+}, or indeed jointly with Fe^{2+} itself

$$RoLH^+ + Fe^{III}L + M^{n+} \rightleftharpoons RoLFe^{3+} + ML^{(n-3)+} + H^+ \qquad (28a)$$

$$RoLH^+ + Fe^{III}L + Fe^{2+} \rightleftharpoons RoLFe^{3+} + FeL^- + H^+ \qquad (28b)$$

These reactions may conveniently be regarded as combinations of eq 2 and 3 with the redistribution equilibria

$$RoLM^{n+} + Fe^{III}L \overset{^{\dagger}K_M}{\rightleftharpoons} RoLFe^{3+} + ML^{(n-3)+} \qquad (29a)$$

$$RoLFe^{2+} + Fe^{III}L \overset{^{\dagger}K_{Fe}}{\rightleftharpoons} RoLFe^{3+} + FeL^- \qquad (29b)$$

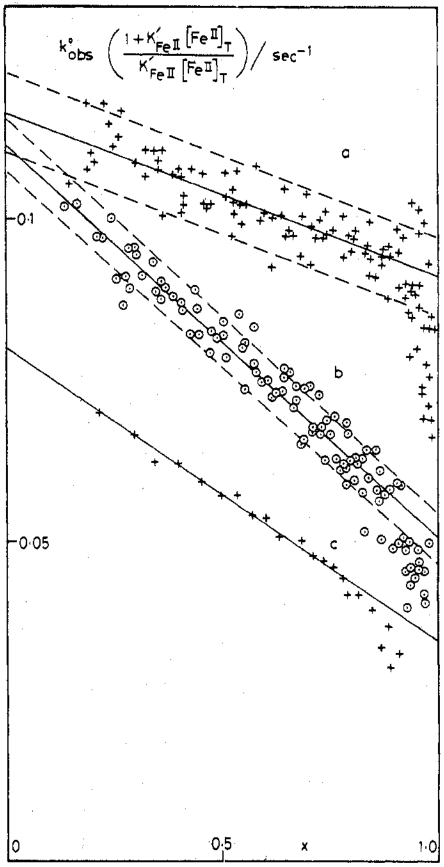

Figure 3. Deviations from first-order kinetics (see Table VIII) showing effects of added nitrilotriacetic acid and Co^{2+} ion and initial concentrations $[L]_F$ and $[Co^{2+}]_0$, respectively: (a) $[L]_F = 3.0$ mM, $[Co^{2+}]_0 = 0$; (b) $[L]_F = 0$, $[Co^{2+}]_0 = 0$; (c) $[L]_F = 0$, $[Co^{2+}]_0 = 4.0$ mM. The straight lines are fitted by least squares to the data from $x = 0$ to $x = 0.9$; the limits are set at ±2 standard errors of estimate.

where the constants $^{\dagger}K$ are the appropriate ratios of stability constants of the complexes involved. The kinetic consequences are interesting but we shall not explore them in full; our experiments were confined to three limiting cases.

(i) Fe^{2+} and Co^{2+} in Excess. In this case deviations from first order are entirely due to the release of iron(III). It may then be shown that

$$k_{\text{obsd}}/k^0{}_{\text{obsd}} = 1 - 2x/(1 + \sqrt{1 + 4x(1 - x)(K^{-1} - 1)}) \tag{30}$$

where x, k_{obsd}, and $k^0{}_{\text{obsd}}$ are as defined above and

$$K = \frac{{}^{\dagger}K_{\text{Fe(II)}}{}^{*}K_{\text{Fe(II)}}[\text{Fe}^{2+}]\{\text{H}^+\}^{-1} + {}^{\dagger}K_{\text{Co}}{}^{*}K_{\text{Co}}[\text{Co}^{2+}]\{\text{H}^+\}^{-1}}{1 + {}^{*}K_{\text{Fe(II)}}[\text{Fe}^{2+}]\{\text{H}^+\}^{-1} + {}^{*}K_{\text{Co}}[\text{Co}^{2+}]\{\text{H}^+\}^{-1}} \tag{31}$$

${}^{*}K_{\text{Co}} = K_{\text{Co}}K_{\text{a2}}$, and ${}^{*}K_{\text{Fe(II)}} = K_{\text{Fe(II)}}K_{\text{a2}}$. Typical curves[28] are shown in Figure 4. For comparison with experiment we note that K is fairly insensitive to $[\text{Co}^{2+}]$; using typical values of the other parameters K increases by 20% as $[\text{Co}^{2+}]$ goes from 20 to 67 m*M*. Data from five experiments all lie close to the curve for $K = 0.14$.

(ii) No Inhibitor Present Initially. The effect in these experiments may be illustrated by calculating out a typical example. When $[\text{Fe}^{2+}] = 66.4$ m*M* initially and pH is 3.245, we obtain $\alpha = 0.34$, assuming inhibition by Co^{2+} only, with equilibrium constants from Table I. Using eq 29 in addition, with $K = 0.14$, we obtain $\alpha = 0.52$, compared with the experimental $\alpha = 0.52$ (Table VIII and Figure 3, curve b).

(iii) Addition of Complex $\text{Fe}^{\text{III}}\text{L}$. When iron(III) and nitrilotriacetic acid are added in equivalent amounts at the start of the reaction, eq 29 require a lowering of the initial specific rate, given by

$$\frac{k^0{}_{\text{obsd}}}{k^{00}{}_{\text{obsd}}} = \frac{K(a + b)}{2a(1 - K)}\left[-1 + \sqrt{1 - \frac{4(1 - K)ab}{K(a + b)^2}}\right] \tag{32}$$

where $k^0{}_{\text{obsd}}$ and $k^{00}{}_{\text{obsd}}$ are initial specific rates observed with and without added complex, a and b are initial concentrations of cobalt(III) and $\text{Fe}^{\text{III}}\text{L}$, and K is given by eq 31. The results of two such experiments (Table IX) are consistent with K of the order of 0.04. This is lower than the previous estimate but may in fact be more correct. A direct calculation of K from the data of Table I, using eq 31, yields $K = 0.066$, though again with some uncertainty since it involves combining equilibrium data for different temperatures and ionic strengths.

E. Possible Bimolecular Pathway. As stated above, eq 11 is equivalent to a mixed first- and second-order rate law and could therefore arise from parallel first- and second-order pathways, due for example to a bimolecular process

$$\text{RoLFe}^{2+} + \text{RoLFe}^{2+} \xrightarrow{k_2} \text{RoLFe}^{3+} + \text{Co}^{2+} + \text{FeL}^- \tag{33}$$

However this would not explain why the apparent second-order term diminishes with added H_3L, nor is it consistent with the kinetics. In terms of eq 11, the fraction of the observed rate of reaction contributed by the second-order term is α at $x = 0$, declining to zero at $x = 1$. It then follows that in any series of experiments where $k^0{}_{\text{obsd}}$ varies because of varying RoLFe^{2+} concentration, the second-order fraction should vary also. For example, given $\alpha = 0.6$ when $k^0{}_{\text{obsd}} = 17 \times 10^{-3}$ sec^{-1}, we calculate $\alpha = 0.43$ when $k^0{}_{\text{obsd}} = 6.3 \times 10^{-3}$ sec^{-1}, but no such trend in α values is seen (Table VIII). Moreover in one such experiment the initial cobalt(III) concentration was halved without any significant effect on either $k^0{}_{\text{obsd}}$ or α (Table VIII). It is clear that bimolecular reactions are relatively unimportant though the present arguments do not exclude some small fraction of the observed reaction proceeding by such a pathway. The different estimates of K might suggest this; but further experiments would be needed to establish a reliable upper limit for k_2.

Table VIII. Deviation from First-Order Kinetics: Cobalt(II)-Inhibited Reactions[a]

$10^3 \times$ $[\text{Co}^{\text{III}}]_0$, *M*	$10^3 \times$ $[\text{L}]_{\text{F}}$, *M*	$10^3 \times$ $[\text{Co}^{2+}]_{\text{T}}$, *M*	$10^3 \times$ $k^0{}_{\text{obsd}}$, sec^{-1}	α
	pH 3.245, $[\text{Fe}^{\text{II}}]_0 = 66.4$ m*M*			
3.0	0.0	0.0	67.9[b]	0.54
3.0	0.0	2.0	52.6	0.54
3.0	0.0	4.0	46.8	0.56
3.0	1.0	0.0	72.9	0.16
3.0	2.0	0.0	70.0	0.22
3.0	3.0	0.0	70.3	0.20
3.0	4.9	0.0	66.3	0.15
1.5	24.0	0.0	13.6[c]	0.04
	pH 2.90, $[\text{Fe}^{\text{II}}]_0 = 80.0$ m*M*			
3.0	0.0	20.0	17.4	0.61
3.0	0.0	26.7	15.1	0.56
3.0	0.0	33.3	12.6[d]	0.66
1.5	0.0	33.3	12.7	0.67
3.0	0.0	53.2	8.7	0.61
3.0	0.0	66.6	6.3	0.64

[a] Parameters $k^0{}_{\text{obsd}}$ and α are defined by eq 11. Temperature 25°; total glycine 0.50 *M*; ionic strength 1.0 *M* (NaClO_4). $[\text{Co}^{\text{III}}]_0$ is the initial cobalt(III) concentration; $[\text{L}]_{\text{F}}$ is the concentration of added free nitrilotriacetic acid. [b] Average of two experiments. [c] $[\text{Fe}^{2+}]_{\text{T}} = 22.3$ m*M*. [d] Average of five experiments.

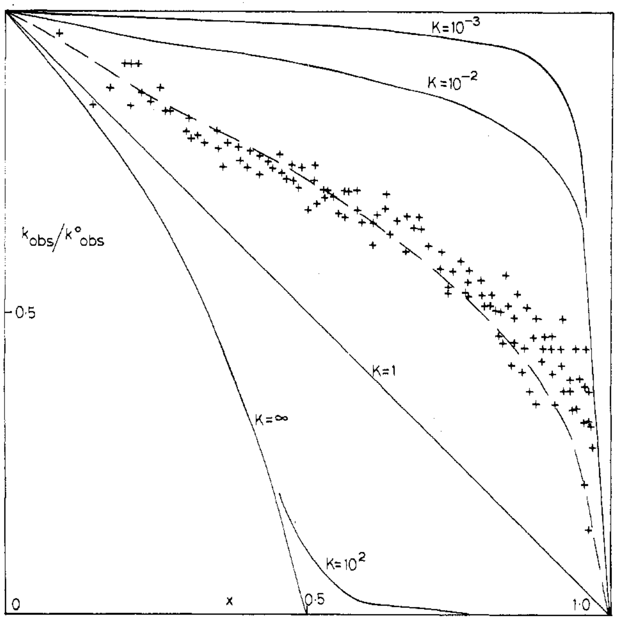

Figure 4. Rate data plotted according to eq 30. Experiments in glycine buffer, pH 2.90, with excess Co^{2+} ion (Table VIII). The broken curve corresponds to $K = 0.14$; other curves correspond to values of K as shown.

IV. Spectrum of the Complex RoLFe^{2+}. This was obtained at 0°, at which temperature the half-life is approximately 4 min (Figure 1). In the region above 400 nm absorbance measurements were made on several identical mixtures, scanned over successive short wavelength ranges. Below 400 nm the spectrum was rapidly obscured by the very intense absorbance of the iron(III) product. For each measurement a fresh mixture was prepared and the absorbance obtained by extrapolating back to zero time. It is clear

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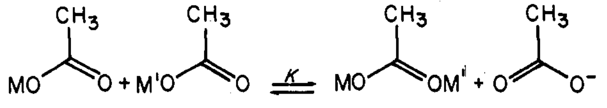
[28] The curves all have the useful feature that pairs of points at $x = {}^1/_2 \pm d$ (where d has any value from 0 to ${}^1/_2$) are collinear with the point at $x = 0$, which justifies our treatment of the data by the linear eq 11.

Table IX. Effect of Added Nitrilotriacetatoiron(III) on Reactions in Glycine Buffer[a]

$10^3 \times$ $[\mathrm{Co^{III}}]_0$, M	$10^3 \times$ $[\mathrm{Fe^{III}L}]_0$, M	$10^3 \times$ k^0_{obsd}, $\mathrm{sec^{-1}}$	$k^0_{\mathrm{obsd}}/k^{00}_{\mathrm{obsd}}$ Obsd	Calcd (eq 32) $K = 0.01$	$K = 0.04$	$K = 0.10$
3.0	0.0	12.5 ± 0.5				
3.0	1.5	11.3 ± 0.5	0.9 ± 0.1	0.94	0.88	0.83
3.0	3.0	10.4 ± 0.5	0.8 ± 0.1	0.91	0.83	0.76

[a] Temperature 25°; pH 2.90; total glycine 0.50 M, ionic strength 1.00 M ($\mathrm{NaClO_4}$); $[\mathrm{Fe^{II}}]_\mathrm{T} = 80.2$ mM, $[\mathrm{Co^{II}}]_\mathrm{T} = 33.3$ mM.

Table X. Equilibrium Constants for Redistribution Reactions



M	M'	log K^d	Ref
$\mathrm{H^+}$	$\mathrm{H^+}$	−11	*a*
$\mathrm{Cr^{3+}}$	$\mathrm{H^+}$	−5.4	*a, b*
$\mathrm{Co(NH_3)_5{}^{3+}}$	$\mathrm{H^+}$	−5.3	*a, c*
$\mathrm{Ag^+}$	$\mathrm{Ag^+}$	−4.1	*a*

[a] Reference 24. [b] E. Deutsch and H. Taube, *Inorg. Chem.*, 7, 1532 (1968). [c] M. B. Barrett, J. H. Swinehart, and H. Taube, *ibid.*, **10**, 1983 (1971). [d] Temperature 25°; various ionic strengths.

that over the accessible wavelength range the spectrum of the complex is similar to that of its constituent chromophores; the peak at 500 nm coincides within experimental error with that of $\mathrm{RoLH^+}$, and the intensity (ϵ 77 M^{-1} $\mathrm{cm^{-1}}$) is only slightly greater than that of $\mathrm{RoLH^+}$ (70 M^{-1} $\mathrm{cm^{-1}}$). It was observed in a separate experiment that FeL', the complex of N-methyliminodiacetic acid,[16] has negligible absorption at this wavelength ($\epsilon < 2$ M^{-1} $\mathrm{cm^{-1}}$). Thus in the nomenclature of Robin and Day[29] $\mathrm{RoLFe^{2+}}$ is a "type I" complex with no appreciable intervalence charge transfer between the metal ions.

Discussion

I. Identity of the Precursor Complex. There is little doubt that the complexes RoLM^{n+}, including $\mathrm{RoLFe^{2+}}$, exist predominantly in the tridentate form (structure I, eq 35 below). Wherever the comparison is possible, K_M is similar to the value for the complex of the same metal with N-methyliminodiacetic acid and quite different from that of the glycine or nitrilotriacetic acid complex (Table I).[30] Moreover the titration experiments on $\mathrm{RoLNi^{2+}}$ and the kinetic measurements on $\mathrm{RoLFe^{2+}}$ also rule out the monodentate or bidentate forms since free carboxyl groups would be protonated at pH 3 or below.[31-34] It does not follow however that I is the precursor complex in the strict sense of eq 1. The alternative possibilities may be summarized as follows.

(a) The two-step mechanism 34 is consistent with the rate law provided that the intermediates achieve steady-state concentrations. In acidic media this pathway is ruled out

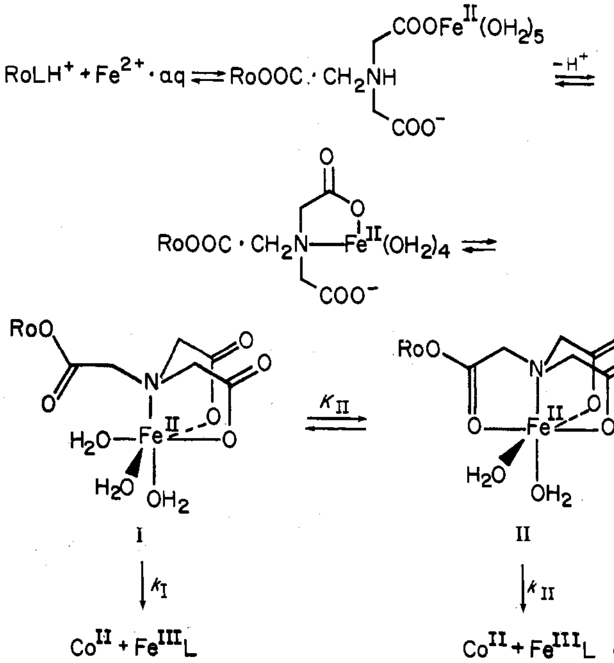
$$\mathrm{RoLFe^{2+} \rightarrow RoOH_2{}^{3+} + FeL^-} \tag{34a}$$

$$\mathrm{RoOH_2{}^{3+} + FeL^- \rightarrow products} \tag{34b}$$

by direct experiment: below pH 1.0 reaction 34b is too slow to account for the observed rate of the $\mathrm{RoLH}_n{}^{n+} + \mathrm{Fe^{2+}}$ reaction. At lower acidities (pH >2.5) reaction 34b becomes complete within the time of mixing the solutions, so that step 34a would have to be rate determining; but analogous reactions with nonreducing divalent metal ions (Table II) are slower than electron transfer by a factor of 10^6.

(b) A bimolecular process $\mathrm{RoL + Fe^{2+}}$ is consistent with the rate law (eq 16), but it requires a very high specific rate, $k_1 K_{\mathrm{Fe(II)}} = 1.0 \times 10^5$ M^{-1} $\mathrm{sec^{-1}}$ at 25°. (Compare the specific rates of $\mathrm{Fe^{2+}}$ reductions of $\mathrm{RoCl^{2+}}$, 1.35×10^{-3} M^{-1} $\mathrm{sec^{-1}}$,[35] and $\mathrm{RoC_2O_4{}^+}$, 0.43 M^{-1} $\mathrm{sec^{-1}}$.[36] It is difficult to see how the ligand $\mathrm{L^{3-}}$ can promote electron transfer so efficiently unless its chelating function is somehow involved.

(c) Since chelation is generally a stepwise process, the rate-determining step could be displacement of water from $\mathrm{Fe^{2+}}$·aq by one of the entering ligand groups (eq 35). But it cannot be either the first, second, or third such displacement, since, if so, the tridentate complex I could not be appreciably formed, and the value of $K'_{\mathrm{Fe(II)}}$ (eq 17) would be less than we observe.



(35)

(d) Granted that I is the predominant species, other binuclear complexes in equilibrium with it might offer more

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(29) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

(30) Against this it might be argued that the positive charges of the cobalt(III) center will tend to repel the incoming M^{n+} ion, so that the measured K_M is less than expected on purely structural considerations. However the upper limit for such an effect is indicated by the comparative proton affinities of RoL and $\mathrm{CH_3N(CH_2COO)_2{}^{2-}}$, log $K_\mathrm{H} = 8.0$ and 9.3, respectively (Table I). Metal ion affinities are generally less sensitive to charge effects than are proton affinities[13] and it remains most unlikely that the RoLM^{n+} complexes considered here have more than two chelate rings.

(31) Compare the complexes of EDTA ($\mathrm{H_4Y}$) with free carboxyl groups: $\mathrm{NiYH^-}$, $\mathrm{p}K_\mathrm{a} = 2.20$;[32] $\mathrm{Co(YH)Br^-}$, $\mathrm{p}K_\mathrm{a} = 2.96$;[33] and a complex of nitrilotriacetic acid, NiLH, $\mathrm{p}K_\mathrm{a} = 3.1$.[34]

(32) G. Anderegg, *Helv. Chim. Acta,* 47, 1801 (1964).

(33) W. C. E. Higginson and M. P. Hill, *J. Chem. Soc.*, 1620 (1959).

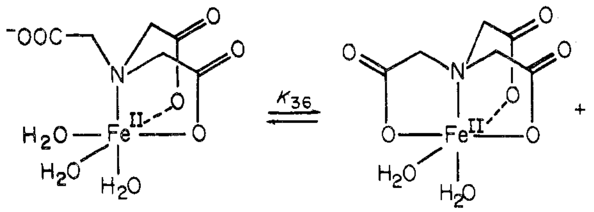
(34) N. Tanaka and M. Kimura, *Sci. Rep. Tohoku Univ., Ser. 1,* **50**, 203 (1967).

(35) J. H. Espenson, *Inorg. Chem.*, 4, 121 (1965).

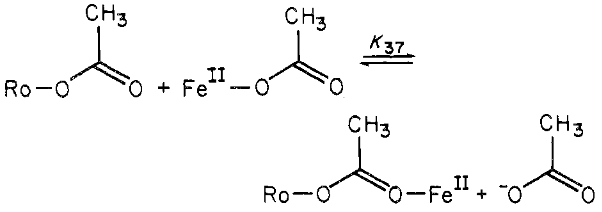
(36) C. Andrade and H. Taube, *Inorg. Chem.*, 5, 1087 (1966).

favorable electron-transfer pathways. Thus monodentate and bidentate precursors can be considered, but again it is difficult to see why they should be more effective than structure I. The choice therefore lies between "direct" electron transfer across the space between the metal centers in structure I or a further water-replacement step to yield the quadridentate intermediate II. If the latter is involved, it is clear from the low value of k_1 that water replacement is not rate limiting; hence we may postulate a rapid equilibrium between I and II.

If complex II is the electron-transfer precursor, its lifetime depends on the equilibrium constant K_{II} which can be roughly estimated by considering the separate factors which go to determine it. These are closure of a five-membered ring and formation of an iron(II)-carboxyl linkage, offset by the repulsive effect of the bound pentaamminecobalt(III) group. Thus K_{II} is expected to be similar to the product $K_{36}K_{37}$ of equilibrium constants for the reactions



(36)



(37)

A value $K_{36} \approx 10^{2.2}$ may be inferred from stability sequences of chelate complexes with varying numbers of rings.[37] Estimation of K_{37} is more difficult but a lower limit can be obtained by inspection of some analogous reactions involving bridging carboxyl. It is evident (Table X) that intercation repulsion decreases with decreasing acidity of the cation. $H^+ > Cr^{3+} \gtrsim Co(NH_3)_5{}^{3+} > Ag^+$, from which we estimate $K_{37} \gg 10^{-5}$, whence $K_{II} \gg 10^{-3}$ and $k_{II} \lesssim 100\ \text{sec}^{-1}$ at 25°. The point at issue here is not so much the absolute value of k_{II} as the fact that, whether the precursor complex is represented as I or II, its lifetime with respect to electron transfer is still much greater than the typical residence times of ligands attached to iron(II).[38,39]

II. Comparison with Second-Order Process. As reported elsewhere[19] we have also studied the following reaction involving the same metal ions in the same immediate ligand environments

$$(NH_3)_5Co^{III}O\cdot COCH_3{}^{2+} + CH_3N(CH_2COO)_2Fe^{II} \rightarrow Co^{2+} + CH_3N(CH_2COO)_2Fe^{III+} \qquad (38)$$

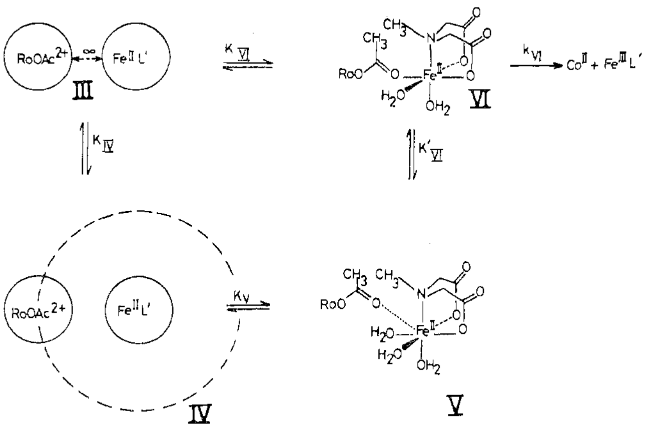


Figure 5.

The rate term is $k_2'[RoOAc^{2+}][FeL']$, where L′ is the anion of *N*-methyliminodiacetic acid, consistent with the expected bimolecular mechanism. Under the same conditions as the present work (25°, ionic strength 1.0 *M* ($NaClO_4$), glycine buffer), $k_2' = 1.4 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$. This leads to an interesting comparison between first-order and second-order rate processes. In Figure 5, state III denotes $RoOAc^{2+}$ and FeL′ in solution at infinite separation, and VI the presumed immediate precursor complex with Co^{III} and Fe^{II} joined by a carboxyl bridge. Assuming that the first-order rate constants k_{II} and k_{VI} are similar, the ratio of measured rate constants is determined by the ratio of preequilibrium constants K_{II} (eq 35) and K_{VI} (Figure 5)

$$k_1/k_2' = K_{II}/K_{VI} \qquad (39)$$

which is simply the ratio of formation constants of a chelate and a nonchelate complex, other things being approximately equal. The nature of the chelate effect has been discussed by Schwarzenbach[40] and Martell,[41] who concluded that where a five-membered ring is involved the ratio K_{II}/K_{VI} is expected to be of the order of 10^2 *M*. This corresponds fairly well with our observed ratio $k_1/k_2' = 82$ *M*.

Alternatively, it is possible to envisage the preequilibrium as a sequence of three steps: first the approach of oxidant and reductant to position IV having the same interionic distance as in the binuclear species, then a mutual reorientation to bring the ferrous ion into the vicinity of the acetate group (position V), and finally the establishment of the carboxyl bridge in the complex VI (Figure 5). From molecular models, the average cobalt-iron distance in I is found to be approximately 6.5 Å. At this distance the interaction between the cobalt and iron complexes in the association complex IV may be neglected and the formation constant estimated on a purely statistical basis. In Figure 5 the $RoOAc^{2+}$ and $Fe^{II}L'$ complexes[16] are represented as spheres of similar radius, and another sphere is shown, concentric with $Fe^{II}L'$ and passing through the center of $RoOAc^{2+}$. We then have

$$K_{IV} = LV \cong 1\ M^{-1} \qquad (40)$$

where *L* is Avogadro's constant and *V* is the volume enclosed between the dotted sphere and the boundary of the iron(II) complex. And since we define species V to be similar to I as regards the relative positions of the two metal ions we have $K_{VI}'k_{VI} = k_1$, while $K_{IV}K_VK_{VI}'k_{VI} = k_2'$; hence $K_V = 0.0125$. Thus, even when the species $RoOAc^{2+}$ and FeL′ have

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[37] Along the series of Fe(II) complexes with glycine, *N*-methyliminodiacetic acid, and nitriloacetic acid, stability constants increase as log K_M = 4.3, 6.65, and 8.84, respectively; and with ethylenediamine-*N,N*-diacetic acid and ethylenediamine-*N,N,N′,N′*-tetraacetic acid, they are 9.81 and 14.3, respectively (all values quoted at 20°, ionic strength 0.01 or 0.10 *M*).[24] In other words, stability increases regularly by about 2.2 log units for each additional acetic acid unit.

[38] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37, 307 (1962).

[39] M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 58 (1965).

[40] G. Schwarzenbach, *Helv. Chim. Acta*, 35, 2344 (1952).

[41] A. E. Martell, *Experientia, Suppl.*, No. 9, 52 (1964).

diffused to the required mutual distance, the probability of their being in the correct relative orientation is approximately 1.25%.

Thus the comparison of rates of the two reactions is consistent with the assumptions that the only significant difference between them is an outer-sphere association process of the type IV → V and that in both reactions the bulk of the electron transfer takes place over the shortest possible distances.

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Cobalt(III) Complexes of 4,7-Dimethyl-1,4,7,10-tetraazadecane. Preparations, Stereochemistry, and Reactions and the Effect of N-Methylation on Relative Isomer Stabilities

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The preparations of complexes [Co(4,7-dimetrien)X$_2$]$^{n+}$ (4,7-dimetrien = 4,7-dimethyl-1,4,7,10-tetraazadecane; X = Cl, OH$_2$, NO$_2$; 2X = CO$_3$) are described. The configurations of the racemic geometric isomers are assigned as *RR,SS*-α or *RR,SS*-β from pmr spectra and from interconversion reactions in which configurational changes at the asymmetric nitrogen donor centers are precluded by the methyl substituents. The following conversions occurring with isomerization have been observed: β-dichloro → α-dichloro; β-dichloro → α-dinitro; β-chloroaquo → α-chloroaquo; β-diaquo → α-diaquo; β-diaquo → α-dinitro; α-dichloro → β-carbonato. From the tendency for β → α isomerizations to occur and from other comparisons with the corresponding [Co(trien)X$_2$]$^{n+}$ complexes, it is evident that the methyl substituents enhance the stabilities of the "angular" configuration at the central amine donor atoms (stability α > β) such that trans complexes with this ligand might not be obtainable.

Introduction

The chemistry of diacidocobalt(III) complexes with the flexible tetradentate ligand triethylenetetramine,[1] [Co(trien)X$_2$]$^{n+}$, and with homologs of trien, has attracted considerable interest and the field has been reviewed recently.[2]

Apart from the alternative trien ligand topologies,[3] alternative configurations are possible at the asymmetric secondary nitrogen donor centers giving rise to two possible configurational isomers *RR,SS* and *RS,SR*[4] for each of the β and trans topologies. Figure 1 shows all the possible isomers (one optical form of each) for complexes [Co(trien)X$_2$]$^{n+}$ having identical substituents X. In addition, further geometric isomers β_1 and β_2 are possible when the diacido substituents are not identical in [Co(trien)XY]$^{n+}$, and with the exception of *RS*-trans, all of these isomeric forms have now been isolated and characterized for various diacido and amino acid complexes of trien having the above formula types.[5–11] The less stable *RS*-trans configuration has however been obtained for the first time recently[12] in the complex *RS-trans*-[Co(*meso*-3*R*,8*S*-dimetrien)Cl$_2$]ClO$_4$[1] where the particular dispositions of the methyl substituents on the trien backbone impose stereospecificity at the coordinated secondary nitrogen centers.

The present paper examines the isomers which may be realized for cobalt(III) complexes when the trien ligand is modified by methyl substitution at the central nitrogen atoms to create two tertiary amine functions (Figure 1).

It has been shown that the secondary N-H bonds of coordinated trien may exert considerable effect in determining the stereochemical course of various reactions.[13] Thus formation of the diaquo,[7] amino acid,[10,11] chloroammine,[14] and dinitro[15] complexes in *RS*-β[4] forms requires inversion at the "planar" secondary nitrogen center of the *RR*-β configuration. These inversions occur by N-H hydrogen exchange favored by more alkaline conditions. Similarly racemization of Δ-*RR*-β-

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(1) trien = triethylenetetramine = 1,4,7,10-tetraazadecane. It has become customary to designate alkyl-substituted derivatives according to the positions of substitution on the tetraazadecane chain for which the trivial designation trien is retained; thus 4,7-dimetrien = 4,7-dimethyl-1,4,7,10-tetraazadecane.

(2) G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).

(3) The three possible topological arrangements for coordination of trien about an octahedral metal center have usually been designated (arbitrarily) as α, β, and trans. The alternative nomenclature symmetrical cis and unsymmetrical cis for the α and β topologies in *cis*-diacido complexes has been suggested by J. H. Worrell and D. H. Busch, *Inorg. Chem.*, 8, 1563 (1969).

(4) The *R* or *S* specifications refer to the absolute configurations at asymmetric carbon atoms or at the secondary nitrogen centers of the coordinated trien ligand, according to the sequence rules of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966). For β complexes the configuration at the normal trigonal nitrogen ("angular" nitrogen) is designated before the nitrogen center bridging the two coplanar chelate rings (the "planar" nitrogen). Δ and Λ refer to the absolute chelate configurations about the metal atom as defined in *Inorg. Chem.*, 9, 1 (1970).

(5) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 4, 45 (1965).

(6) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 787 (1967).

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(8) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967).

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(12) M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, 45, 1443 (1972).

(13) G. H. Searle and A. M. Sargeson, *Inorg. Chem.*, 12, 1014 (1973).

(14) M. Dwyer, unpublished work.

(15) G. H. Searle and F. R. Keene, unpublished work.