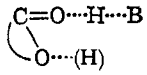
tion state (A) with two water molecules and the catalyst species, and a transition state (B) of the type below where the (H) refers to a proton present only for acid catalysis.



To obtain Table IV several assumptions were made for the fractionation factors of the transition states. For the cyclic states all hydrogens were assumed equivalent in each case. For the conventional states (B), a sort of stepwise assignment was used. In all cases, 0.55 was used for ϕ_2, *i.e.*, the value obtained from k_D/k_H for acetate ion catalysis. For acetic acid this then leads to $\phi_3 = 0.707$, a value which in turn was accepted for the hydronium ion reaction. These are not necessarily the best values in every case; they do, however, give a consistent set of factors.

In terms of data-fitting there is no strong preference for one kind of transition state relative to the other. The B-type is perhaps slightly preferable for acetate ion and hydronium ion catalyses but slightly poorer for the water reaction. A possibly more significant point is that the B-type seems almost inescapably to lead to ϕ_2 values which are so low as to make interpretation of them very difficult in terms of equilibrium acid–base data and behavior. A different kind of comment is that, even with the simplified approach of equivalent hydrogens, the cyclic transition states are reasonably satisfactory, a result which then permits other kinds of evidence to be adduced in their support.

The Chromium(II) Reductions of Some Cobalt(III) Aquoammine Complexes[1]

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Abstract: The rate of Cr(II) reduction ($\mu = 1$, $NaClO_4$) of *cis*- and *trans*-diaquo- and -aquoamminebis(ethylenediamine)cobalt(III) ions has been found to follow the rate law $R = k[Co(III)][Cr(II)][H^+]^{-1}$. The temperature dependence of the acidity constants of the substrates has been measured. Second-order rate constants at 25° (M^{-1} $sec^{-1} \times 10^{-6}$) and energies of activation (kcal/mole) for the reduction of the hydroxo complexes are: aquo complexes, *cis* 0.79, 6.4; *trans* 2.6, 2.6; ammine complexes, *cis* 0.20, 6.2; *trans* 0.22, 2.4. The small effect of *trans* H_2O relative to the effect noted in similar Fe(II) systems has been interpreted on the basis of less reorganization within the binuclear complex for the Cr(II) reduction. The variation of activation energies for the Cr(II) reductions may be interpreted on the same basis or as an effect on the formation of the binuclear complex.

Reduction of Cr(III) or Co(III) by Cr(II) usually proceeds *via* a binuclear transition state M(III)–X–Cr(II) if the trivalent complex contains a group, X, capable of binding two metals at once.[2] The dependence of the rate of reduction on the nature of the groups present in the transition state has been examined in some detail.[2–5] This paper is concerned with the influence of the nonbridging ligands of the trivalent ion.

In 1956, Orgel proposed[6] that the field strength of the ligand *trans* to the bridging group should be a dominating factor. This followed from the assumption that the incoming electron enters the nonbonding d_{z^2} orbital, the energy of which would be expected to be more seriously affected by variation in field strength of the *trans* ligands than by a similar variation for the *cis* ligands. More recently[2,5] it has been emphasized that outward motion of the *trans* ligand should lower the energy of the d_{z^2} orbital and thereby facilitate electron transfer.

We now report the kinetics of Cr(II) reduction of the ions *cis*- and *trans*-$Co(en)_2(H_2O)_2^{+3}$ and *cis*- and *trans*-$Co(en)_2(NH_3)H_2O^{+3}$,[7] the object being to observe the effect of H_2O and NH_3 in both stereochemical positions relative to the bridge.

Experimental Section

***trans*-Hydroxoaquobis(ethylenediamine)cobalt(III) Perchlorate (tO).** This was prepared by a modification of the method of Basolo and Steninger.[8] A 15-g portion of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride[9] was heated in 15 ml of water for a few minutes and passed through Amberlite IRA-400 (hydroxide form). The effluent, not exceeding 30 ml was made just acid with 72% perchloric acid, and treated with pyridine (5 ml). The solid was purified twice by dissolving in the minimum quantity of 1 *N* perchloric acid and titrating to pH 3.5 with 10 *N* NaOH,[10] yield 4.7 g. The *cis* salt is not precipitated under these conditions.

Anal. Calcd for $[Co(en)_2(H_2O)(OH)](ClO_4)_2$: C, 11.6; H, 4.60; N, 13.6. Found:[11] C, 12.0; H, 4.83; N, 13.5.

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[1] Presented in part before the Chemical Society of Washington, College Park, Md., May 1965.

[2] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[3] Effect of bridging groups: J. P. Candlin, J. Halpern, and O. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[4] Nonbridging ligands on Cr(II): (a) J. B. Hunt and J. E. Earley, *ibid.*, **82**, 5312 (1960); (b) R. D. Cannon and J. E. Earley, to be published.

[5] P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

[6] L. E. Orgel in "Quelques Problemes de Chimie Minerale," Institute Solvay, Brussels, 1956, p 289.

[7] Complexes will be called cO, tO, cN, tN, or generally, ROH_2^{+3} or ROH^{+2}; en is ethylenediamine.

[8] F. Basolo and D. H. Steninger, *J. Am. Chem. Soc.*, **72**, 5748 (1950).

[9] J. C. Bailar and C. L. Rollinson, *Inorg. Syn.*, **2**, 222 (1946).

[10] W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

[11] Analyses by Schwarzkopf Microanalytical Laboratory, Inc.

***cis*-Hydroxoaquobis(ethylenediamine)cobalt(III) Bromide (cO).** A stirred suspension of 4.3 g of carbonatobis(ethylenediamine)-cobalt(III) bromide[12] in 6 ml of water was treated dropwise with concentrated HBr until all dissolved to a neutral solution, and 5 ml of pyridine was added. The product separated after stirring at 0°. It was recrystallized twice by dissolving in a little dilute HBr and adding pyridine, yield 7.0 g from 24.6 g of carbonato complex.

Anal. Calcd for $[\mathrm{Co(en)_2(H_2O)(OH)}]\mathrm{Br_2 \cdot H_2O}$: C, 12.2; H, 5.4; N, 14.3. Found: C, 12.5; H, 5.06; N, 14.2.

***cis*-Bromoamminebis(ethylenediamine)cobalt(III) Bromide.** A mixture of 8.5 g of *trans*-dibromo bromide, prepared from the carbonato bromide by Werner's method,[12] and 5 g of crushed ice was stirred mechanically in an ice bath while the calculated quantity of concentrated aqueous ammonia was slowly added (0.5 hr). After standing at room temperature for 5 min, the mixture was filtered and the product washed with ethanol and ether. It was used in the next stage without further purification.

***trans*-Aquoamminebis(ethylenediamine)cobalt(III) Bromide (tN).** The *cis*-bromoammine bromide was dissolved in its own weight of water and treated dropwise with cold saturated lithium hydroxide solution, with stirring and ice cooling. The product was separated from the more soluble *cis* isomer by adding concentrated HBr. It was reprecipitated from water by adding ethanol until the spectrum in 1 *M* perchloric acid became constant (and identical with that given by Nyholm and Tobe[13]). By titration, the product was found to contain 14%, by weight, of the hydroxo complex.

Anal. Calcd for 86% $[\mathrm{Co(en)_2(NH_3)H_2O}]\mathrm{Br_3 \cdot H_2O}$–14% $[\mathrm{Co(en)_2(NH_3)OH}]\mathrm{Br_2}$: C, 10.6; H, 4.94; N, 15.4. Found: C, 11.0; H, 5.19; N, 15.10.

***cis*-Chloroamminebis(ethylenediamine)cobalt(III) Dithionate.** This was prepared[14] by treating 3.0 g of the dichloro chloride, finely powdered, with 2.0 ml of concentrated aqueous ammonia. The slurry evolved heat and became semisolid. Ethanol (0.5 ml) was added and the mixture filtered. The brown solid was washed with ethanol, stirred with 8 ml of water, and filtered into aqueous sodium dithionate, yield 0.8 g of quite pure, insoluble product.

***cis*-Aquoamminebis(ethylenediamine)cobalt(III) Perchlorate (cN).** The bromide of the desired complex was prepared easily by Werner's method[15] but was found to decompose on standing, even in darkness, to a red, sparingly soluble solid, probably $[\mathrm{Co(en)_2(NH_3)Br}]\mathrm{Br_2}$. Therefore, the perchlorate was prepared as follows. The *cis*-chloroamminodithionate (11.0 g) and fresh silver hydroxide (20 g) were stirred into 16 ml of water for 30 min at 45°. The product was filtered into an ice-cooled solution of 4 g of lithium perchlorate in 75 ml of EtOH. After stirring overnight at 0°, the product was washed with absolute ethanol and dry ether, yield 7.3 g. To purify, the complex (7 g) was dissolved in 12 ml of water and 2.2 ml of ethanol added to cause some precipitation. The mixture was filtered into a solution of 4 g of lithium perchlorate in 50 ml of absolute alcohol and 25 ml of dry ether, yielding an oil which solidified when triturated with absolute ethanol and ether. Further recrystallizations followed by adding alcohol and ether to the saturated aqueous solution, until the absorption spectrum remained constant, final yield 2.3 g. The product was found to contain 21% by weight of the hydroxo form.

Anal. Calcd for 79% $[\mathrm{Co(en)_2NH_3)H_2O}](\mathrm{ClO_4})_3 \cdot \mathrm{H_2O}$–21% $[\mathrm{Co(en)_2(NH_3)OH}](\mathrm{ClO_4})_2$: C, 9.4; H, 4.47; N, 13.7. Found: C, 10.5; H, 5.08; N, 14.6.

Other Materials. Sodium perchlorate solutions were prepared by adding sodium hydroxide (Baker Analytical grade) to sufficiently diluted perchloric acid (G. F. Smith Co.). Commercial sodium perchlorate has been found to contain impurities which oxidize Cr(II). Chromium(II) solutions were prepared by reducing aqueous chromium(III) perchlorate (G. F. Smith) with amalgamated zinc in the presence of sufficient $\mathrm{NaClO_4}$ to give the desired ionic strength. Cr(II) was analyzed separately with each experiment by oxidizing with acid dichromate and determining the excess Cr(VI) iodometrically.[16]

Kinetic Measurements. Reactions were carried out in 10-cm optical cells with rubber serum caps, secured with wire. The caps were separated from the solution by means of "parafilm" and the tops greased with vaseline after being punctured. Nitrogen, scrubbed by passing through a Cr(II) solution, was passed for 1 hr or more before adding Cr(II), using plastic inlet needles. The pressure in the cell remained positive throughout each experiment. Temperature was controlled within ±0.2° by circulating water through a double-walled cell holder. Reactions were started by injecting Cr(II) from a syringe with platinum needle, and, after vigorous shaking, followed by decrease in absorbance at 274 (tO) or 490 mμ (other complexes), using a Cary 14 recording spectrophotometer. At 274 mμ, it was possible by fast manipulation to make the first reading at $t = 5$ sec, but at 490 mμ, readings were affected by froth in the cell until about $t = 20$ sec. The data were treated according to the second-order rate law

$$\frac{-\mathrm{d}[\mathrm{Co(III)}]}{\mathrm{d}t} = k[\mathrm{Co(III)}][\mathrm{Cr(II)}] \tag{1}$$

using the integrated form

$$y = \log\left[(D_0 - D_\infty) - \frac{a}{b}(D_0 - D)\right] - \log(D - D_\infty) = 0.434(b - a)kt \tag{2}$$

where D_0, D, are D_∞ are optical densities at times 0, t, and ∞, and a and b are initial reagent concentrations ($a < b$). Since the absorbance of Cr(II) is negligible at the wavelengths used, D_0 could be measured prior to injection of Cr(II). D_∞ was obtained from the recorder trace by inspection.

Cr(II) was taken in excess and, in many cases, the residue was determined when reaction was complete. Usually, the reaction was found to be nonstoichiometric; Cr(II) consumed exceeded Co(III) taken, sometimes by as much as a factor of 2. The source of the anomaly was not traced, but some empirical observations are worth recording. (i) Losses were greater with Cr(II) solution prepared by electrolysis of $\mathrm{Cr(ClO_4)_3}$, than with the zinc-reduced solutions. (ii) The anomaly was much less in sulfate or chloride than in perchlorate media. (iii) It tended to increase with the over-all time of the experiment. (iv) It was greater in the more dilute Cr(II) solutions. In separate experiments, it was established that there was some loss of reducing power whenever Cr(II) was diluted with perchloric acid. This was not serious at concentrations above 10^{-3} *M*, however. The simplest explanation is perhaps that the perchloric acid contained a small proportion (0.03%) of some material capable of oxidizing Cr(II) under the influence of the Co(III)–Cr(II) oxidation–reduction reaction.

When the loss of Cr(II) exceeded about 30%, the plot of y *vs.* t became curved, and all such runs were rejected. In the tO experiments, with more dilute Cr(II), stoichiometry was not checked, but the constancy of k over a range of initial Cr(II) concentration shows that losses were not serious during the short time of the experiments. In other cases, losses were the same at both temperatures, and we conclude that the measured activation energies are not seriously affected by the side reaction.

Isomerization of the substrates in the acidic solutions studied is slow, so that this reaction does not complicate the reductions. The spectra of the substrate solutions did not change appreciably during the deaeration procedure so that prior isomerization is not a difficulty.

Measurement of Acid Dissociation Constants. A Beckman Model 76 expanded-scale pH meter was used with glass electrode and calomel reference electrode in which the KCl salt bridge had been replaced with saturated NaCl solution. This was necessary since the unmodified electrode gave erratic results when used in concentrated perchlorate media, probably owing to the formation of insoluble $\mathrm{KClO_4}$ in the porous plug. The meter was standardized using Beckman buffer solutions (of pH 4.01 and 6.85 at 25°) with appropriate temperature corrections. Solutions and electrodes were thermostated to ±0.2°.

Aquoammine Complexes. Solutions of the complexes in a suitable excess of acid were titrated with carbonate-free sodium hydroxide. Measurements near to the half-neutralization point were taken on the expanded scale of the pH meter (readable to ±0.002 pH). There was no detectable change of pH with time.

Diaquo Complexes. Although the species $\mathrm{Co(en)_2(H_2O)_2}^{+3}$ and $\mathrm{Co(en)_2(OH)_2}^{+}$ are relatively inert, the intermediates $\mathrm{Co(en)_2(OH)H_2O}^{+2}$ isomerize quite rapidly[17] at room temperature, so that the above procedure could not be applied. Titrations were simulated as follows. The complexes were dissolved in 1 *M* $\mathrm{NaClO_4}$

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[12] A. Werner, *Ann.*, **386**, 1 (1912) (pp 72, 73).

[13] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

[14] A. Werner, *Ber.*, **44**, 1887 (1911).

[15] Reference 12, p 187.

[16] J. V. Prestia and J. E. Earley, to be published.

[17] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

Table I. Rates of Chromium(II) Reduction of Cobalt(III) Complexes in Perchlorate Media (1 *M*)

		Initial concentration, *M*				
Complex[a]	Temp, °C	[Cr(II)] $\times 10^4$	[Co(III)] $\times 10^4$	[H$^+$]	k, M^{-1} sec^{-1}	k_1,[b] sec^{-1}
cO	29.9	103	16.5	0.992	1.23	1.22
	29.9	42	16.5	0.502	2.36	1.18
	29.9	42	11.1	0.195	5.24	1.02
	29.9	20	15.3	0.099	11.6	1.15
						Mean 1.14 ± 0.07
cO	6.9	216	24.6	0.958	0.238	0.228
	7.0	183	28.6	0.488	0.390	0.190
	7.0	92	27.6	0.195	1.05	0.205
	7.1	66	26.2	0.099	1.99	0.197
						Mean 0.205 ± 0.015
tO	27[c]	1.80	0.44	1.03	99	102
	27[c]	2.20	0.44	1.03	90	93
	27[c]	2.92	0.43	1.03	89.6	93
	27[c]	3.63	0.43	1.03	99	102
						c
tO	29.9	1.85	0.44	1.03	98	101
	29.9	1.85	0.44	0.78	119	93
	29.9	1.85	0.44	0.63	147	93
	29.9	1.85	0.44	0.53	171	91
						Mean 94.5 ± 4
tO	7.0	1.61	0.46	1.03	21.8	22.5
	7.0	1.61	0.46	0.53	43	22.7
	7.0	1.61	0.46	0.29	85	24.4
						Mean 23.2 ± 0.8
cN	30.0	66.5	19.2	1.00	0.218	0.218
	30.0	24.5	11.4	0.49	0.598	0.296
	30.0	30	8.7	0.20	1.31	0.263
	30.0	32	8.3	0.106	2.46	0.261
						Mean 0.26 ± 0.03
cN	6.8	168	20.1	0.933	0.053	0.0495
	7.0	168	21.5	0.470	0.090	0.0423
	7.0	145	22.7	0.191	0.199	0.0380
	6.9	114	23.0	0.103	0.378	0.0389
						Mean 0.038 ± 0.002[d]
tN	29.8	46.7	9.2	0.970	0.607	0.589
	29.8	45.4	8.9	0.486	1.20	0.583
	29.8	22.7	9.0	0.198	2.91	0.576
	29.8	18.7	9.8	0.101	6.01	0.608
						Mean 0.59 ± 0.01
tN	7.0	171	13.4	0.969	0.154	0.149
	7.0	166	13.1	0.487	0.287	0.140
	7.0	88	12.0	0.194	0.736	0.143
	7.0	69	14.9	0.099	1.299	0.129
						Mean 0.14 ± 0.01

[a] cO is *cis*-$Co(en)_2(H_2O)_2^{+3}$, cN is *cis*-$Co(en)_2(NH_3)(H_2O)^{+3}$; tO and tN are the *trans* complexes. [b] Errors listed are standard deviations: M. J. Moroney, "Facts from Figures," 3rd ed, Penquin, Baltimore, Md., 1956. [c] Room temperature; not included in calculations of E_2. [d] For the cN system only, the best rate law is $k = 0.01 + 0.038[H^+]^{-1}$. The standard deviation for a one-term rate law $k = 0.042[H^+]^{-1}$ is 0.004.

containing a suitable amount of acid. When the temperature was steady, a certain amount of base was added quickly, and the change of pH with time was noted. The change in [H$^+$] was approximately first order and extrapolation gave the pH at zero time. From three or four such measurements, the value of pK_a was interpolated as the pH at half-neutralization. At 2-3°, the isomerization of the hydroxoaquo complexes was almost negligibly slow; at 45°, it was too rapid to follow. The second acidity of the diaquo ions was not studied.

Results

The dependence of k on acidity may be expressed as $k = k_1[H^+]^{-1}$. Values of k and k_1 are listed in Table I. Table II lists our results on the acid dissociation equilibria, and in Table III these are compared with previous reports. Martin and Tobe[18] determined K_a for *trans*-$[Co(en)_2(NH_3)(H_2O)](NO_3)_3$ at 20°, and studied the kinetics of rearrangement to the *cis*-aquoamine as a function of [H$^+$] and temperature. Their data yield an approximate heat of hydrolysis ΔH_a = 8 ± 1 kcal/mole, in good agreement with the more pre-

Table II. Acid Dissociation of Cobalt(III) Aquo Ions in Perchlorate Media ($\Sigma[ClO_4^-]$ = 1 *M*)

Complex	Temp, °C	pK_a[a]
cO	3 ± 0.5	6.34
	28.2	5.93
tO	2 ± 0.5	5.02[b]
	28.2	4.49[b]
cN	1.3	6.55
	29.0	5.95
	44.2	5.73
tN	1.3	6.25
	28.4	5.65
	44.4	5.38

[a] Estimated errors less than or equal to 0.02 pH unit except for tO. [b] ±0.05 pH unit.

(18) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

Table III. Equilibrium and Rate Parameters (μ = 1.0 ($NaClO_4$), 25°)

Complex[a]	pK_a	ΔH_a, kcal/mole	k_1, sec^{-1}	E_1, kcal/mole	$k_2 \times 10^{-6}$, M^{-1} sec^{-1}	E_2, kcal/mole
cO	5.98[b]	6.2 ± 0.8	0.80	12.6 ± 1.3	0.79 ± 0.07	6.4 ± 2.1
tO	4.55[b]	7.7 ± 1.2	0.72	10.3 ± 0.9	2.6 ± 0.3	2.6 ± 2.1
cN	6.05	7.9 ± 0.5	0.178	14.1 ± 1.4	0.20 ± 0.02	6.2 ± 1.9
tN	5.70[c]	8.2 ± 0.5	0.44	10.6 ± 0.9	0.22 ± 0.01	2.4 ± 1.4

[a] See footnote *a*, Table I. [b] Compare the values cO (6.05) and tO (4.45) obtained in 1 M $NaNO_3$ (ref 17). [c] Compare the value 5.68 derived from Martin and Tobe's result[18] by means of the temperature dependence reported here.

cise value given here. Bjerrum and Rasmussen[17] studied the hydrolysis of the *cis*- and *trans*-diaquo complexes by a technique similar to the present one, and also measured the kinetics of interconversion of the *cis* and *trans* isomers spectrophotometrically under various conditions.[19] They noted that the rate of racemization varied markedly from one sample to another. Our materials reacted somewhat more rapidly ($t_{1/2} \sim 10$ min) than those of Bjerrum and Rasmussen (30 min, estimated from the pH–time data given in their paper). This may account for discrepancies of the order of 0.1 log unit, our results being closer to the equilibrium pK_a in both cases. But it is not clear how far the comparison between results in the two different media, sodium nitrate and sodium perchlorate, is valid.[20]

Table III lists the second-order rate constants, k_2, for the Cr(II) reduction of the conjugate bases of the aquo ions and the corresponding activation energy E_2. For $Cr(NH_3)_5OH^{+2}$, k_2 and E_2 may be computed as 2.1×10^6 M^{-1} sec^{-1} and 5.1 kcal/mole.[21,22]

Discussion

The O^{18} tracer experiments of Kruse and Taube[19] have shown that one oxygen atom is transferred to Cr in the Cr(II) reduction of the *cis*-diaquo complex under conditions similar to those of our experiments. This demonstrates that electron transfer proceeds *via* a singly bridged activated complex. This is consistent with the kinetic results, which may be interpreted according to eq 3, where R refers to the $Co(en)_2NH_3$ or $Co(en)_2H_2O$. It is possible that a bridged inter-

$$RH_2O^{+3} \overset{K_a}{\rightleftharpoons} ROH^{+2} + H^+ \qquad (3a)$$

$$ROH^{+2} + Cr^{+2} \xrightarrow{k_2} \text{products} \qquad (3b)$$

mediate is formed during reaction 3b, as has been discussed in some detail by Taube.[2] To take account of this, reaction 3b may be rewritten

$$ROH^{+2} + Cr^{+2} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (R\overset{H}{O}Cr)^{+4} \qquad (4)$$

$$(R\overset{H}{O}Cr)^{+4} \xrightarrow{k_4} \text{products} \qquad (5)$$

Assuming that the concentration of the intermediate reaches a steady state, the second-order rate constant, k_2, is then

$$k_2 = \frac{k_3k_4}{k_{-3} + k_4}$$

If the equilibrium 4 is set up relatively rapidly, $k_2 = k_3k_4/k_{-3} = K_3k_4$. Equilibrium constants $^*\beta_{12}$ of certain hydrolytic polymers $[M_2OH]^{+(2n-1)}$ have been measured, which, combined with the acidity constants $^*K_1$, yield equilibrium constants K_{12} for the reaction

$$M^{+n} + MOH^{+(n-1)} \overset{K_{12}}{\rightleftharpoons} (M\overset{H}{O}M)^{+(2n-1)} \qquad (6)$$

analogous to eq 4 above. Table IV shows that K_{12} is fairly constant over a wide range of heavy metals. Then provided that there is no special stability due to the presence of two different valence states, a reasonable estimate for K_3 would then be 0.1 to 10 M^{-1} whence $k_4 = 10^{6\pm1}$ sec^{-1} for the *trans*-aquo species, the fastest reacting complex.

Table IV. Equilibrium Parameters for Binuclear Complex Formation (Eq 7)[a]

M^{+n}	−Log $^*K_1$	−Log $^*\beta_{12}$	Log K_{12}
Hg^{+2}	3.55	2.67	0.88
Cr^{+3}	3.86		−1.13
Th^{+4}	4.3	2.9	1.4
Be^{+2}	6.5	3.5	3.0
Pb^{+2}	7.8	6.3	1.5
Zn^{+2}	9.1	8.1	1.0
La^{+3}	10.1	9.95	0.15
Cd^{+2}	10.2	9.10	1.1

[a] Data from L. G. Sillén and A. E. Martell, Ed., "Stability Constants," Special Publication No. 17, The Chemical Society; London, 1964, except for Cr^{+3}: G. Thompson, Ph.D. Thesis, University of California, 1964, UCRL-11410.

Merideth,[23] working in Connick's laboratory, has assigned a lower limit of 7.5×10^9 sec^{-1} to the rate constant, k_r, involved in the temperature dependence of the transverse relaxation time of O^{17} in acidic aqueous solutions (at 25°) containing chromous ion (ΔH_r^* = 3 kcal/mole). The model which Merideth favors is a rapid inversion process for the chromous ion, related to k_r, and a still more rapid exchange of axial water molecules. If $10^{6\pm1}$ sec^{-1} is a reasonable estimate for k_4, then the electron-transfer step is considerably slower than the processes studied by Merideth. However, it is by no means certain that k_r can be identified with k_3 and/or k_{-3}, and as Candlin and Halpern[24] point out, the possibility of some rate-limiting process being involved in reaction 4 should not be overlooked.[25]

If, as seems likely, $k_{-3} >> k_4$, our observation that the activation energies E_2 decrease in the order cO ≈ cN ≈ $Co(NH_3)_5OH^{+2}$ > tO ≈ tN might be due to

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(19) See also W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **82**, 526 (1960).

(20) J. B. Hunt and D. Wolcott, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 380.

(21) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

(22) D. J. Bearcroft, D. Sebera, A. Zwickel, and H. Taube, quoted in ref 21.

(23) C. W. Merideth, Ph.D. Thesis, University of California, 1965 (UCRL-11704).

(24) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

(25) See also M. Anbar and D. Meyerstein, *Nature*, **206**, 818 (1965).

variation in ΔH_3, the heat term corresponding to K_3 (reaction 4).[12] Such reactions seem to be primarily entropy controlled, but the magnitude of the difference in E_2 between the *trans* isomers and the other systems is not large, 4 ± 2 kcal/mole. Steric effects are known to be important in ion association.[26]

Table V compares our results with those of Benson and Haim[5] on the Fe(II) reductions of the chloro complexes analogous to the hydro complexes we have reduced with Cr(II). The bridge mechanism is established for the Cr(II) reductions of cO by the O^{18} tracer work of Kruse and Taube.[19] The same mechanism is supported for the Fe(II) reductions of the chloro complexes by analogy with the $CoCl^{+2}$–Fe(II) reaction studied by Conocchioli, Nancollas, and Sutin.[27]

Table V. Kinetic Data for Reduction of *cis*- and *trans*-Aquo and -diaquoamminebis(ethylenediamine)cobalt(III) Complexes in Perchlorate Media (1 *M*)

	Cr(II) reductant (X⁻ = OH⁻, 25°)		Fe(II) reductant (X⁻ = Cl⁻, 25°[5])
Oxidant	$k_2 \times 10^{-6}$, M^{-1} sec^{-1}	E_2, kcal/mole	$k_2 \times 10^4$, 25°[5])
cis-$Co(en)_2(H_2O)X^{+2}$	0.79	6.4	4.6
trans-$Co(en)_2(H_2O)X^{+2}$	2.6	2.6	2400
cis-$Co(en)_2(NH_3)X^{+2}$	0.20	6.2	0.18
trans-$Co(en)_2(NH_3)X^{+2}$	0.22	2.4	0.66

In the Cr(II) reductions, there seems to be no marked correlation of rate with the field strength of the *trans* ligand. The rate of reduction of the *trans*-aquo complex is somewhat larger than the other rates in the Cr(II) series, but much larger in the Fe(II) series. This implies that if outward motion of the *trans* ligand is involved, it is much more important in the slower Fe(II) reductions. This agrees with the low isotopic fractionation factor for the *trans* nitrogen observed in Co(III)–Cr(II) reductions.[28] Since the activation energies, E_2, are the same for *trans*-aquo and *trans*-ammine oxidants, the relatively small increase in rate for the Cr(II) reduction of the *trans*-aquo species must reside in an entropy effect, possibly involved with partial release of the water molecule into the solvent sheath.[29] The small difference between the activation energies of Cr(II) reductions of oxidants which have a chelated nitrogen atom *trans* to the bridge and those with a monodentate ligand in that position might be taken to agree with the suggestion that the chelate attachment restrains motion of the nitrogen atom.[28] This is an alternative to the possible steric effect on formation of the binuclear complex mentioned earlier.

It may be concluded that factors involved with outward motion of the *trans* ligand may not be totally absent in the Co(III)–Cr(II) system, but they are much less important than in the Co(III)–Fe(II) reductions which proceed at slower rates.

The rates of Cr(II) reduction of the $Co(en)_2(NH_3)OH^{+2}$ oxidants are about 10^{10} faster than the rates of Fe(II) reductions of the $Co(en)_2(NH_3)Cl^{+2}$ oxidants. Since Cl^- and OH^- are rather similar in reactivity in Co(III)–Cr(II) reactions,[21,28] the principal difference between the two systems resides in the difference of about 1.2 v. (27.6 kcal/mole) in the potentials of the Cr(II) → Cr(III) and Fe(II) → Fe(III) couples. For a pair of outer-sphere electron-transfer reactions for which all factors other than difference in free energy of reaction are either unimportant or constant, Marcus' theory predicts[30] as a first approximation[31]

$$\log \frac{k_{\mathrm{Cr(II)}}}{k_{\mathrm{Fe(II)}}} \approx \frac{1}{2}\,\frac{\Delta(\Delta F)}{2.30RT} = 10$$

It is of some interest that the same factor is observed for these inner-sphere reactions.

Comparison of the Cr(II) → Cr(III) and Fe(II) → Fe(III) couples, using the customary cyclical formalism and available $\Delta H°$ data[32] indicates that the difference in reducing power between Cr(II) and Fe(II) may be rationalized in terms of factors related to the difference in symmetry of the electron removed in the oxidation of these reductants. The possible importance of this symmetry difference in determining the relative efficiency of bridging halide ions for Cr(II) and Fe(II) reductions has been discussed by Diebler and Taube.[33] They suggest that the electron from Cr(II) may be transferred through a σ interaction, whereas Fe(II) may involve interactions of π symmetry. The effect of *trans* ligands on the rate might be expected to be affected by such a difference in detailed electron-transfer mechanism.

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(27) T. J. Conocchioli, G. Nancollas, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 1453 (1964).

(28) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

(29) M. Levine, T. Jones, W. Harris, and W. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961).

(30) R. Marcus, *J. Chem. Phys.*, **43**, 679 (1965); *J. Phys. Chem.*, **67**, 853 (1963).

(31 For such a large value of $\Delta(\Delta F)$ terms involving more complex dependence on $\Delta(\Delta F)$ should be important.

(32) W. Latimer, Ed., "Oxidation Potentials," 2nd ed, Prentice-Hall Inc., New York, N. Y., 1952, pp 221, 246.

(33) H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).