

# Outer-Sphere Electron-Transfer Reactions of Macrocyclic Complexes of Cobalt(III). A Critical Assessment of Linear Free Energy Relations<sup>1</sup>

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**Abstract:** Outer-sphere Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and V<sup>2+</sup> reductions of several complexes of the type *trans*-Co<sup>III</sup>LX<sub>2</sub> (L = a tetradentate macrocyclic ligand) have been examined. For the majority of these oxidants, it is possible to use electrochemical information to estimate the standard reduction potentials of the cobalt(III)–cobalt(II) couples and thus the standard free energy of reaction, Δ*G*<sup>°</sup>. An experimental correlation of the form Δ*G*<sup>‡</sup> = *a* + *b*Δ*G*<sup>°</sup> + ... seems applicable to each reducing agent, with *b* slightly larger than the theoretically predicted 0.5; the experimental parameters *a* are only weakly dependent on the nature of the cobalt oxidant and in fact do not depend as strongly as predicted (*e.g.*, by Marcus) on the intrinsic reorganizational parameters (Marcus' λ) as estimated from the self-exchange reactions of cobalt(III)–cobalt(II) couples.

The study of the electron-transfer reactions of coordination complexes has posed some striking challenges to our understanding of the fundamentals of chemical kinetics. On the experimental side, it has been possible to design reactant systems in which interaction between metal centers is minimized (outer-sphere mechanism). A recent and important variation is the development of macrocyclic ligand systems which ensure a minimal change in the coordination environment of the metal during the electron-transfer process. Therefore, the key reaction step involves simply the transfer of charge between metal centers.<sup>3</sup> The reactions can be simple enough that detailed theoretical analyses have been attempted.<sup>4</sup> A particularly fascinating feature of this class of reactions is the fact that the range of reactivities is so large; *i.e.*, rates can be changed by as much as a factor of 10<sup>9</sup> by merely changing the ligands associated with one of the reactant metals.<sup>5</sup>

Although theories based on rate-limiting Franck-Condon restrictions have seemed reasonably successful, systematic tests<sup>4–6</sup> of these theories have in fact been restricted to fairly limited classes of reactants. For example, the Marcus treatment eventually results in a simple functional relationship (1) between activa-

$$\Delta G_{12}^{\ddagger} \cong \frac{\lambda_{12}}{4} + \frac{\Delta G_{12}^{\circ}}{2} + \frac{(\Delta G_{12}^{\circ})^2}{4\lambda_{12}} \quad (1)$$

(1) (a) In its initial stages at Boston University, this research was partially supported by the National Science Foundation (Grants No. GP 34673 and GP 7549). More recently at Wayne State University, this research has been supported in part by the Public Health Service (Grant No. AM-14341). We gratefully acknowledge this support. (b) Taken in part from the Ph.D. dissertation of R. C. Patel, Boston University, 1969.

(2) Wayne State University.

(3) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

(4) For useful reviews of theoretical discussions, see (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964); (b) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966.

(5) For recent reviews, see (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967; (b) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970; (d) J. E. Earley, *Progr. Inorg. Chem.*, **13**, 243 (1970).

(6) (a) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963); (b) R. J. Campion, N. Purdie, and N. Sutin, *ibid.*, **3**, 1091 (1964); (c) N. Sutin, *Annu. Rev. Nucl. Sci.*, **12**, 285 (1962).

tion and thermodynamic parameters<sup>7</sup> (where λ is the intrinsic reorganized barrier required to achieve the nuclear configuration of the activated complex and the subscripts 1 and 2 are used to distinguish oxidant and reductant where appropriate). The experimental verifications of (1) have most systematically explored the relation between Δ*G*<sub>12</sub><sup>‡</sup> and Δ*G*<sub>12</sub><sup>°</sup>, with only a few attempts to ascertain the experimental dependence on λ or the physical significance of λ.<sup>4–8</sup> In this context it has been a source of frustration that electron-transfer reactions of the Werner complexes of cobalt(III) could not be used to examine the functional form of (1), since (1) these complexes have probably been the most exhaustively investigated; (2) the reactions of these complexes exhibit the greatest variation rate with change of coordinated ligand; and (3) in the two or three cases that comparisons have been possible with functions of the type (1), it is reactions of such cobalt(III) complexes which seem most often deviant from the theoretical models.<sup>6a,9,10</sup>

A more limited but useful approach to linear free energy relations in electron-transfer reactions of cobalt(III) complexes has been developed recently. For example, if we consider complexes of the type CoN<sub>4</sub>LX (where N<sub>4</sub> indicates four amine or NH<sub>3</sub> ligands, X has available nonbonding electrons and can function as a "bridging" ligand, and L is any other ligand), then one may distinguish variations in reactivity which arise for different potential bridging ligands X from variations in reactivity which occur as only a "nonbridging" ligand, say L, is varied from oxidant to oxidant.<sup>11–13</sup> Thus it has been shown that the relative reactivities of

(7) (a) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963); (b) *ibid.*, **72**, 891 (1968).

(8) (a) D. R. Stranks, *Discuss. Faraday Soc.*, No. **29**, 73 (1960); (b) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience, New York, N. Y., 1960, p 78.

(9) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

(10) G. Davies, *Inorg. Chem.*, **10**, 1155 (1971).

(11) R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968).

(12) (a) C. Bifano and R. G. Linck, *ibid.*, **89**, 3945 (1967); (b) *Inorg. Chem.*, **7**, 908 (1968); (c) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969); (d) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970); (e) *ibid.*, in press.

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

cobalt(III) oxidants with different "bridging" ligands X are similar for outer-sphere reductants<sup>9,11,14</sup> but differ widely for inner-sphere reductants.<sup>9,11,14-17</sup> Yet similar relative reactivities are observed for both inner-sphere and outer-sphere reductants if the bridging ligand X is held constant and the nonbridging ligands L are varied.<sup>11,12,18,19</sup> In analyzing and systematizing these various reactivity patterns, Linck and co-workers<sup>12</sup> have proposed that the rate constants  $k_a$  and  $k_b$  for reduction of  $\text{CoN}_4\text{LX}$  (for X constant, L variable) by reducing agents a and b are related by

$$\log k_a = \alpha_X \log k_b + \beta_{X,a,b} \quad (2)$$

Some evidence has been acquired that as the reducing agents a become more powerful (*i.e.*, increasingly negative  $\Delta G^\circ$ )  $\alpha_X$  decreases.<sup>12c,18</sup> However, at the same time it appears that for a change in X (thereby changing the power of the oxidant and of course  $\Delta G^\circ$ ) but holding the reducing agent constant, the very simple relationship 3<sup>12d,e</sup> holds. Whether (3) is applicable for re-

$$\log k_{a,X} = (\alpha' = 1) \log k_{a,X'} + \beta_a \quad (3)$$

ductants more powerful than  $\text{Fe}^{2+}$  is still an open question. However, comparison of eq 1, 2, and 3 raises the unexpected possibility that  $\Delta G_{12}^\circ$  varies with  $\Delta G_{12}^\circ$  in so complicated a manner that the dependence is different if the variations in  $\Delta G_{12}^\circ$  are accomplished through change of reductant rather than through change of oxidant. Thus our previous attempt<sup>11</sup> to discover a general free energy correlation similar to (1) may be complicated by factors more fundamental than the varying stabilities of precursor complexes.<sup>20</sup>

One of the most serious limitations which has arisen in the quest for free energy relations in this class of reactions, or indeed even in examination of the crudest questions involving the range of reactivities exhibited by cobalt(III) complexes, has been the lack of approximate methods for estimating reduction potentials for most of the cobalt(III)-cobalt(II) couples involved. To the present it has been impossible to unambiguously ascribe the varying reactivities of  $\text{CoN}_4\text{LX}$  com-

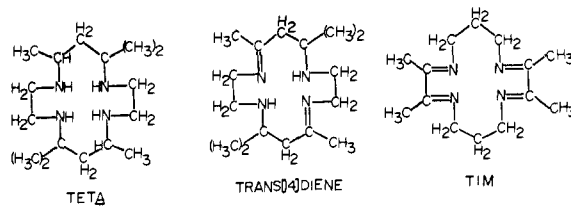


Figure 1. Macrocyclic ligands (see ref 26 and 38).

plexes either to the stretching of cobalt-ligand bonds necessary to achieve the geometry of the activated complex,<sup>3,5,11,21,22</sup> or to the variations in rate expected<sup>4-6,10,11,13,23</sup> to accompany the changes in  $\Delta G_{12}^\circ$ . Thus, even the work of Sutin and his collaborators,<sup>17,24</sup> which has elegantly documented the contributions to  $\Delta G_{12}^\circ$  and to  $k_{12}$  which arise from the differing stabilities of isomeric products, has not succeeded in some quantitative comparisons partly due to the unaccountable changes in  $\Delta G_{12}^\circ$  contributed by the different cobalt oxidants.

The present study was initiated a few years ago, originally to explore in greater depth some ideas concerning the reactivity of cobalt(III)-fluoride complexes.<sup>11</sup> A detailed analysis of acid-dependent reactivities of the  $\text{Co}^{\text{III}}(\text{en})_2\text{LF}$  complexes (reported here) did not seem entirely compatible with the cobalt-ligand stretching model proposed by Patel and Endicott,<sup>11</sup> but these reactivities were qualitatively compatible with estimates of the variations in the potentials of the appropriate cobalt(III)-cobalt(II) couples based on a crystal-field model proposed by Rock<sup>25</sup> at about the same time.

Two very recent developments in these laboratories have prompted the major line of inquiry represented by this report. Endicott<sup>13</sup> demonstrated that Curtis-type<sup>26,27</sup> macrocyclic ligand (Figure 1) complexes of  $\text{Co}^{\text{III}}$  are reduced reversibly<sup>28,29</sup> and that when the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions of these complexes were compared with reductions of  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$ <sup>9,30</sup> and  $\text{Co}(\text{NH}_3)_6^{3+}$ <sup>9,31</sup> the four reactions were in reasonable agreement with (1) (these reactions involve a range of about 12 kcal/mol for  $\Delta G_{12}^\circ$  and about  $10^5 \text{ M}^{-1} \text{ sec}^{-1}$  in  $k_{12}$ ). The second recent development was the discovery by Rillema, *et al.*,<sup>32</sup> that electrochemical reductions of  $\text{Co}^{\text{III}}\text{LX}_2$  complexes were generally "chemically reversible"<sup>33</sup> in nonaqueous solvents and that the corre-

(14) J. P. Candlin, J. Halpern and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

(15) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, No. 29, 42 (1960).

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

(17) (a) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966); (b) *ibid.*, **87**, 4210 (1965).

(18) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).

(19) Note that the reactivities are "similar" only in the restricted sense that (2) holds approximately for a given family of oxidants. Values of  $\alpha_X$  seem to vary with the reducing agent as noted below.

(20) In our attempt<sup>11</sup> to generate a general expression of type (2) we relied on the Marcus cross relation<sup>4</sup>  $k_{12} = \sqrt{k_{11}k_{22}K_{12}}$  to justify factoring the observed rate constant into components due to the oxidant and to the reductant. We also proposed a specific ligand stretching model to account for the different values  $\Delta G_{12}^\circ$  which must result when ligand X is transferred from  $\text{CoN}_4\text{LX}$  to the solvent (outer-sphere reactions) or to the reducing agent (inner-sphere reactions), but we ignored the possibility of differing precursor complex stability constants. Earley<sup>6d</sup> does not seem to have noted either of the latter points in concluding that the success of our correlation "should not be surprising." Earley also argued<sup>6d</sup> that protonation of oxidant amine (or  $\text{NH}_3$ ) ligands may make significant contributions to  $\Delta G_{12}^\circ$ . It does not seem likely that the future of the reaction products can affect the energetics of the electron-transfer step. There is also overwhelming evidence that (unless X is a very basic ligand such as  $\text{OH}^-$  or  $\text{F}^-$ ) the reaction rates are nearly independent of  $[\text{H}^+]^{10,9,11,14,15}$  (in acidic solutions), at least for outer-sphere reactions. That such a suggestion could be made is symptomatic of a problem addressed in this paper; namely, the previous lack of even the crudest basis for estimating the oxidizing ability of the various cobalt(III) complexes.

(21) L. E. Orgel, Proceedings of the 10th Solvay Conference, Institute Solvay, Brussels, 1956, p 289.

(22) See also pp 244-248 of ref 5d and references therein.

(23) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).

(24) D. P. Fay and N. Sutin, *Inorg. Chem.*, **9**, 1291 (1970).

(25) P. A. Rock, *ibid.*, **7**, 837 (1968).

(26) The ligands L employed in this study were *trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and *teta* = 5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradecane.

(27) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(28) That is, the macrocyclic ligands remain associated with cobalt(II) in acidic solution. Thus standard potentials and isotope exchange reaction rates may be determined for the *trans*- $\text{CoL}(\text{OH}_2)_2^{3+,2+}$  couples. Naturally, the axial coordination positions are labile (but see below) in the cobalt(II) complexes. In fact, it should also be noted that the cobalt(II) complexes are (at equilibrium) tetragonal, showing little evidence for "bonding" in the axial positions.<sup>13,29</sup>

(29) L. E. Warner, Ph.D. Dissertation, The Ohio State University, 1968.

(30) R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

(31) W. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952.

(32) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).

(33) The studies were performed using a cyclic voltammometric technique (ref 32; see also Experimental Section). The criterion for

sponding values of  $E_{1/2}$  correlate about as expected<sup>25</sup> with changes in crystal-field strength of the ligands X. We have therefore capitalized on this favorable electrochemical behavior to establish a linear free energy correlation of the type (1) for the  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{V}^{2+}$  reductions of a set of model cobalt(III) complexes.

## Experimental Section

(A) **Preparation of Reagents and Solutions.** The preparation and characterization of most of the macrocyclic complexes have been described in detail elsewhere.<sup>13,32,34-38</sup> The *cis*- $\text{Co}(\text{en})_2\text{ClF}^+$ ,<sup>39</sup> *cis*- $\text{Co}(\text{en})_2(\text{OH}_2)_2\text{F}^{2+}$ ,<sup>39</sup> *trans*- $\text{Co}(\text{en})_2\text{F}_2^+$ ,<sup>39</sup> and  $\text{CoEDTA}^-$ <sup>40</sup> complexes were prepared as described in the literature.  $\text{K}_3\text{Co}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$  was generously provided by Professor S. Kirschner. The new complexes prepared for this study are discussed below.

(1)  $[\text{Co}(\text{TlM})(\text{OH}_2)_2](\text{ClO}_4)_3 \cdot 2.5\text{H}_2\text{O}$ .  $[\text{Co}(\text{TlM})\text{Cl}_2]\text{ClO}_4$ <sup>37,38</sup> was suspended in 40 ml of 0.1 M  $\text{HClO}_4$  solution; 1 N  $\text{AgClO}_4$  (6 ml) was added and the solution heated until all  $\text{AgCl}$  coagulated. The  $\text{AgCl}$  was removed by filtration and the volume of red-orange liquid was reduced to 10 ml. Red-orange crystals precipitated from the solution upon cooling. The crystals became amorphous upon washing with ethanol followed by ether. Analytical data were similar for the amorphous solid and the crystals which were air-dried.

*Anal.* Calcd for  $\text{CoC}_{14}\text{H}_{33}\text{N}_4\text{O}_{16.5}\text{Cl}_3$ : C, 24.48; H, 4.85; N, 8.16; Cl, 15.49. Found: C, 24.40; H, 4.85; N, 7.63; Cl, 16.18.

(2)  $[\text{Co}(\text{TlM})(\text{NH}_3)_2](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ . Under vacuum, approximately 25 ml of liquid  $\text{NH}_3$  was distilled from a sodium ammine solution into a flask containing 1 g of  $[\text{Co}(\text{TlM})\text{Cl}_2]\text{ClO}_4$ . The green dichloro complex became a yellow-brown color after stirring for 15 min. After stirring the suspension for an additional hour, all the ammonia was removed by vacuum distillation. The solid was then suspended in 0.1 M  $\text{HClO}_4$  solution and stirred for 1 hr; excess  $\text{NaClO}_4$  was added to completely precipitate the desired complex.

*Anal.* Calcd for  $\text{CoC}_{14}\text{H}_{39}\text{N}_6\text{O}_{13}\text{Cl}_3$ : C, 25.56; H, 4.91; N, 12.78; Cl, 16.17. Found: C, 26.84; H, 4.88; N, 12.32; Cl, 16.40.

(3)  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$ . This species was generated from  $\text{Co}(\text{TlM})(\text{H}_2\text{O})_2^{3+}$  by reduction with excess  $\text{Cr}^{2+}$  in solutions of pH 2. In acid solutions, this species is stable. The most useful feature of the absorption spectrum for our purposes is the band at 545 nm ( $\epsilon$   $3.45 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ). Spectra of tetraphenylborate salts of  $(\text{Co}(\text{TlM})\text{Cl})^+$  and  $(\text{Co}(\text{TlM})\text{Br})^+$  in nonaqueous media have a similar absorption in the 550-nm region.

Solutions of ruthenium(II) were prepared by reducing recrystallized  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  over zinc amalgam. These ruthenium(II) solutions were used within 2-3 hr of their preparation. Solutions of  $\text{V}^{2+}$  were prepared by reductions of acidic  $(\text{HClO}_4)_2\text{VO}_5^9$  or  $\text{VO}(\text{ClO}_4)_2^9$  over zinc amalgam.

Other chemicals were reagent grade and prepared as described previously.<sup>11,18</sup> Acid concentrations were determined by dilution of standard solutions and/or by pH measurements using Instrumentation Laboratories Model 145 pH meter.

"reversibility" in the present sense was the appearance of a peak in the anodic half-cyclic whose potential was close ( $\pm 0.05 \text{ V}$ ) to that of cobalt(III)-cobalt(II) peak appearing in the cathodic half cycle. The consistent observation of the anodic  $\text{Co}^{\text{III}}\text{LX}_2$  peaks in our systems implies that the cobalt(II) complexes either equilibrate their axial positions more slowly than expected of cobalt(II) or that these complexes have unusually high stability constants. The chemistry of these cobalt(II) complexes is being further investigated, but a few additional comments on these points may be found in the discussion below.

(34) (a) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 967 (1966); (b) *ibid.*, 1827 (1966).

(35) (a) N. Sadasivan and J. F. Endicott, *J. Amer. Chem. Soc.*, **88**, 5468 (1966); (b) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967); (c) J. A. Kernohan and J. F. Endicott, *ibid.*, **9**, 1504 (1970).

(36) J. A. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 6977 (1969).

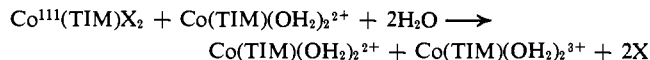
(37) The preparation of  $\text{Co}^{\text{III}}(\text{TlM})\text{X}_2$ <sup>38</sup> complexes was based on information generously provided to us by Dr. Keith Farmery and Professor Daryle H. Busch.

(38) TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.

(39) W. R. Matoush and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 3972 (1956).

(40) A. W. Adamson and K. S. Vorres, *J. Inorg. Nucl. Chem.*, **3**, 206 (1956).

(B) **Procedures for Kinetic Studies.** Syringe techniques which have been described previously<sup>9,11,13</sup> were used for most of the electron-transfer reactions. For some of the faster ( $k > 10^4 \text{ M}^{-1} \text{ sec}^{-1}$ ) reactions we have employed stopped-flow techniques similar to those described previously,<sup>13,18</sup> but using the Durrum or Aminco stopped-flow instruments. To obtain an estimate of the self-exchange rate for  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{3+,2+}$  we have measured the rates of the  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$  catalyzed hydrolyses of  $\text{Co}^{\text{III}}(\text{TlM})\text{X}_2$  ( $\text{X} = \text{NH}_3$  or  $\text{Cl}^-$ )



In the case of  $\text{Co}(\text{TlM})(\text{NH}_3)_2^{3+}$ , the progress of reaction was determined from changes in solution pH (initial pH 3). This reaction proceeded to less than 10% of completion in 48 hours at 25°; there were no significant changes in pH in a similar  $\text{Co}(\text{TlM})(\text{NH}_3)_2^{3+}$  solution maintained for a comparable time period but which did not contain  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$ . In the case of  $\text{Co}(\text{TlM})\text{Cl}_2^+$ , the  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$  catalyzed equilibration was determined from the dependence of the equilibration rate<sup>36c</sup> on  $[\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}]$  and the known stability constants of  $\text{Co}(\text{TlM})\text{Cl}_2^+$  and  $\text{Co}(\text{TlM})(\text{OH}_2)\text{Cl}^{2+}$ ,<sup>41</sup>

(C) **Treatment of Solutions Containing Macrocyclic Complexes.** Many of the  $\text{Co}^{\text{III}}\text{LX}_2$  complexes present unique problems of solubility or complex stability. Several pertinent experimental considerations are outlined below. A problem which is common to all of them is the rapid reaction of  $\text{CoL}^{2+}$  with dissolved oxygen. The efficacy of the deaeration procedures is always manifested in the constancy of the cobalt(III) absorbance following reduction.

(1) *trans*- $\text{Co}(\text{trans}[14]\text{diene})(\text{NH}_3)_2^{2+}$ . This complex was reasonably soluble in  $\text{NaCl}$  but not very soluble in  $\text{NaClO}_4$ . The  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions could be performed in  $\text{NaCl}$  media, but the  $\text{V}^{2+}$  reductions had to be run in  $\text{NaClO}_4$  to avoid  $\text{Cl}^-$  catalysis.<sup>42</sup> Reactions were followed at about 340 nm, near the 320-nm absorbance maximum for  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{2+}$ .<sup>13</sup> Progress of reaction could not be followed at the metal ion absorbance maximum of  $\text{Co}(\text{trans}[14]\text{diene})(\text{NH}_3)_2^{3+}$  ( $\lambda_{\text{max}}$  450 nm) owing to a strong absorbance of the cobalt(II) complex in this spectral region.

(2) *trans*- $\text{Co}(\text{trans}[14]\text{diene})(\text{NO}_2)_2^+$ . This complex was troublesomely unreactive, not very soluble even in  $\text{NaCl}$  solutions, and exhibited an acid-catalyzed aquation. The irreproducibility of the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reduction of this complex was apparently due to the unavoidable presence of some  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)\text{NO}_2^{2+}$  in the reaction mixture. We found that some reaction always occurred in these solutions before our observations commenced. Since solutions with the composition of our reaction mixtures did not exhibit significant changes in their cobalt(III) absorbancies over a period of an hour, we feel that the slowest measured rate constant,  $0.57 \text{ M}^{-1} \text{ sec}^{-1}$ , is probably the best estimate.

(3) *trans*- $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)\text{NCS}^{2+}$ . Since  $\text{Co}(\text{trans}[14]\text{diene})(\text{NCS})_2^+$  is so unstable (stability constant  $\sim 6 \text{ M}^{-1}$ )<sup>36c</sup> we were unable to examine the reactivity of this complex. The rate of reaction of  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)\text{NCS}^{2+}$  was determined in 0.1 M  $\text{NaSCN}$  and in 0.01 M  $\text{NaSCN}$  to ensure that  $[\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{3+}]$  was sufficiently small that it did not present a kinetic complication.

(4) *trans*- $\text{Co}(\text{trans}[14]\text{diene})\text{Cl}_2^+$  and *trans*- $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)\text{Cl}^{2+}$ . These complexes were sufficiently soluble, stable<sup>36c</sup> and reactive that they were a relative pleasure to handle. The reduction of the  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)\text{Cl}^{2+}$  complex was determined at several values of  $[\text{Cl}^-] \leq 5 \times 10^{-3}$  to ensure that  $[\text{Co}(\text{trans}[14]\text{diene})\text{Cl}_2^+]$  and  $[\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{3+}]$  were not kinetically significant.

(5) *trans*- $\text{Co}^{\text{III}}(\text{TlM})\text{X}_2$  Complexes. These complexes are exceptionally easy to reduce to  $\text{Co}(\text{TlM})(\text{OH}_2)_2^{2+}$  and great care must be exercised to avoid contact with extraneous reducing agents (*e.g.*, stainless-steel syringe needles). This is a particularly serious problem with the dihalo complexes.

(D) **Electrochemical studies** were performed as described elsewhere<sup>32</sup> using the Chemtrix SSP-2 three electrode system. In connection with the present report, we attempted to examine the electrochemical behavior of a large number of  $\text{Co}^{\text{III}}(\text{NH}_3)_5\text{X}$  and  $\text{Co}^{\text{III}}(\text{en})_2\text{LX}$  complexes. Many of these complexes proved to be so insoluble in the nonaqueous solvents and prevailing electrolyte (0.1 M tetraethylammonium perchlorate) that we could not obtain even remotely useful information. In all cases, these reductions

(41) D. P. Rillema and J. F. Endicott, manuscript in preparation.

(42) A. Zwicker and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

Table I. Electrode Potentials and Electron-Transfer Rates for the Reduction of Macrocyclic Complexes of Cobalt(III)

Oxidant	$E_{1/2}, V^a$	Meas'd, V	$E^0$	$Ru(NH_3)_6^{2+}$		$V^{2+}$			
				Est'd, V <sup>b</sup>	$k, M^{-1} sec^{-1} c$	$k, M^{-1} sec^{-1} c$	$\mu^d$	$\mu^d$	Log $k^e$
Co( <i>trans</i> [14]diene)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	-0.12 <sup>f</sup>		0.12	3.0 ± 0.4	1.0 <sup>g</sup>	0.48	(0.25 ± 0.01)	0.55	0.02
Co(TIM)(NH <sub>3</sub> ) <sub>2</sub> <sup>3+</sup>	-0.20 <sup>h</sup>		0.05 ± 0.1 <sup>i</sup>	3.7 ± 0.3	1.0	0.57	(0.53 ± 0.01)	0.10	1.07
Co( <i>trans</i> [14]diene)(NO <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	-0.48 <sup>h</sup>		0.17	0.57	0.15 <sup>f</sup>	0.14			
Co( <i>trans</i> [14]diene)(OH <sub>2</sub> )NCS <sup>2+</sup>	-0.32 <sup>h,j</sup>		0.38	11 ± 1	0.10 <sup>g</sup>	1.86			
Co( <i>trans</i> [14]diene)(OH <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	-0.27	0.56	0.53	3.2 ± 0.2	0.010 <sup>g</sup>	1.85	(2 ± 1) × 10 <sup>2,l</sup>	1.0	2.3
Co(TIM)(OH <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	0.54	0.54		(8 ± 1) × 10 <sup>2,l</sup>	0.1	4.24	(1.0 ± 0.1) × 10 <sup>2</sup>	0.12	4.19
Co(tetra)(OH <sub>2</sub> ) <sub>2</sub> <sup>3+</sup>	0.59 <sup>k</sup>	0.59 <sup>k</sup>		(1.9 ± 0.1) × 10 <sup>4</sup>	0.055	5.73	(1.9 ± 0.5) × 10 <sup>2,l</sup>	1.0	3.28
Co(EDTA) <sup>-</sup>	0.60 <sup>m</sup>	0.60 <sup>m</sup>		(3.0 ± 0.5) × 10 <sup>3,l</sup>	0.1	4.88	(7.9 ± 0.1) × 10 <sup>2</sup>	0.12	2.50
Co(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>2-</sup>	0.57 <sup>m</sup>	0.57 <sup>m</sup>		(6 ± 1) × 10 <sup>3</sup>	0.1	3.37	(3.1 ± 0.1) × 10 <sup>4</sup>	0.12	3.30
Co( <i>trans</i> [14]diene)(OH <sub>2</sub> )Cl <sup>2+</sup>	-0.22 <sup>n</sup>		0.49	(2.2 ± 2) × 10 <sup>5</sup>	0.055	3.89	(3.1 ± 0.1) × 10 <sup>3</sup>	0.10	4.05
Co( <i>trans</i> [14]diene)Cl <sub>2</sub> <sup>+</sup>	-0.2		0.45	(3.8 ± 0.4) × 10 <sup>2</sup>	0.1	3.39	(1.7 ± 0.3) × 10 <sup>3</sup>	0.10	4.19
Co(tetra)Cl <sub>2</sub> <sup>+</sup>	-0.12		0.53	(2.0 ± 0.3) × 10 <sup>3</sup>	0.1 <sup>o</sup>	3.71	(6.0 ± 1) × 10 <sup>3</sup>	0.57 <sup>o</sup>	3.39
Co( <i>trans</i> [14]diene)(OH <sub>2</sub> )Br <sup>2+</sup>	-0.06 <sup>n</sup>		0.64	(7.5 ± 0.3) × 10 <sup>4</sup>	0.1	5.0	(1.56 ± 0.09) × 10 <sup>3</sup>	0.12	4.87
Co( <i>trans</i> [14]diene)Br <sub>2</sub> <sup>+</sup>	+0.14		0.79	(5 ± 1) × 10 <sup>6</sup>	1.0 <sup>o</sup>	5.70	(1.2 ± 0.2) × 10 <sup>4</sup>	0.12	4.76
Co(tetra)Br <sub>2</sub> <sup>+</sup>	+0.06		0.71	(1.0 ± 0.3) × 10 <sup>6</sup>	0.57 <sup>o</sup>	6 ± 1	(2.3 ± 0.1) × 10 <sup>4</sup>	0.57 <sup>o</sup>	4.72

<sup>a</sup> Determined in acetonitrile at the stationary platinum electrode *vs.* sce, except as indicated. Reference 29, except as indicated. Uncertainty is ± 0.03 V, except as indicated. <sup>b</sup> Estimated from  $E_{1/2}$  as indicated in the text. See ref 32. <sup>c</sup> Error limits are mean deviations from the mean of two or more determinations. This work, except as indicated (24 ± 1). <sup>d</sup> NaClO<sub>4</sub>, [H<sup>+</sup>] = 10<sup>-3</sup> M, except as indicated. <sup>e</sup> Extrapolation to unit ionic strength using the relation  $\log k = Z_A Z_B f(\mu)$ : J. W. Gryder, *J. Chem. Phys.*, **37**, 718 (1963). The functional dependence on  $\mu$ ,  $f(\mu)$ , was determined from the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reductions of Co(NH<sub>3</sub>)<sub>2</sub>Br<sup>3+</sup> and various Co<sup>III</sup>(en)<sub>2</sub>XY complexes (ref 9 and 11 and R. C. Patel, Ph.D. Dissertation, Boston University, 1969). <sup>f</sup> Determined in water *vs.* sce. <sup>g</sup> NaCl. <sup>h</sup> Irreversible wave. <sup>i</sup> Estimate of  $E^0$  is based on comparison with other Co<sup>III</sup>X<sub>2</sub> complexes. See text. <sup>j</sup> Average of  $E_{1/2}$  for Co(*trans*[14]diene)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup> and Co(*trans*[14]diene)(NCS)<sub>2</sub><sup>2+</sup> (-0.4 V). <sup>k</sup> NaSCN. <sup>l</sup> Reference 12. <sup>m</sup> As cited in ref 24. <sup>n</sup>  $E_{1/2}$  for Co(*trans*[14]diene)(OH<sub>2</sub>)X<sub>2</sub><sup>2+</sup> estimated as average of  $E_{1/2}$  for Co(*trans*[14]diene)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup> and for Co(*trans*[14]diene)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup>. <sup>o</sup> NaBr.

were found to be irreversible either by our criteria<sup>23</sup> (indicating rapid solvolysis of the cobalt(II) products) or by the relative diffuseness of the reduction wave. This irreversibility suggests a significant kinetic component to measured values of  $E_{1/2}$  and makes them an uncertain basis for the estimation of  $E^0$ .

The standard reduction potential,  $E^0$ , for Co(TIM)(OH<sub>2</sub>)<sub>2</sub><sup>3+,2+</sup> was determined from a potentiometric titration of Co(TIM)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup> with Cr<sup>3+</sup> as described elsewhere.<sup>13b</sup>

## Results

Table I summarizes the results of our determination of (1) values for reduction potentials of cobalt(III)-cobalt(II) couples and (2) the second-order specific rate constant for reduction of Co<sup>III</sup>LX<sub>2</sub> complexes by Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> and V<sup>2+</sup>.

The half-wave potentials,  $E_{1/2}$ , cited in Table I were determined in nonaqueous solvents (acetonitrile or DMF). In order to use these measurements to estimate standard reduction potentials, we have assumed that  $E^0 = E_{1/2} + E'$ . The additive constant is largely composed of contributions for the sce (vs. standard H<sub>2</sub>) and the junction potential for our nonaqueous cell system; a smaller contribution (≤ 0.2 V) to  $E'$  seems to arise from variations in electrode potential required to reduce ions of different charge types. To determine values of  $E'$ , we have obtained values of  $E_{1/2}$  in our nonaqueous cell system and values of  $E_{1/2}$  (or  $E^0$ ) in an aqueous cell. Thus we find for 1+ ions that  $E' = 0.65 ± 0.05$  V (based on polarography of Co(*trans*[14]diene)(CN)<sub>2</sub><sup>+</sup> and Co(*trans*[14]diene)CO<sub>3</sub><sup>+</sup>) and for 3+ ions  $E' = 0.80 ± 0.05$  V (based on polarography of Co(*trans*[14]diene)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> and Co(*trans*[14]diene)(OH<sub>2</sub>)<sub>2</sub><sup>3+</sup> and on the value of  $E^0$  for the latter<sup>13</sup>). For dipositive ions, we have used  $E' = 0.70 ± 0.05$  V.

Estimates of potentials for the Co<sup>III,II</sup>(TIM)X<sub>2</sub> couples are very difficult to obtain, as the reductions are irreversible for each of the ligands X tried. We have been able to determine the Co(TIM)(OH<sub>2</sub>)<sub>2</sub><sup>3+,2+</sup> potential from a potentiometric titration. It is to be noted that reversible potentials for the CoL(OH<sub>2</sub>)<sub>2</sub><sup>3+,2+</sup> couples are very similar (0.54, 0.56,<sup>13</sup> and 0.59<sup>13</sup> V for L = TIM, *trans*[14]diene, and tetra, respectively). Furthermore, it seems likely that the irreversibility of the polarographic reductions of Co<sup>III</sup>(TIM)X<sub>2</sub> is a result of very fast solvolysis of the cobalt(II) complexes, analogous to the behavior of the ammine complexes. Thus the irreversible reductions of Co(TIM)(CN)<sub>2</sub><sup>+</sup> (in water and acetonitrile) and Co(TIM)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup> occur at potentials close (± 0.10 V) to those for the quasi-reversible reductions of Co(*trans*[14]diene)(CN)<sub>2</sub><sup>+</sup> and Co(*trans*[14]diene)(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>. With these several considerations in mind, we have estimated that the Co(TIM)(NH<sub>3</sub>)<sub>2</sub><sup>3+,2+</sup> potential is  $E^0 ≈ +0.05 ± 0.1$  V.

Some of the difficulties in handling the various macrocyclic complexes of cobalt(III) have been alluded to in the Experimental Section. Some additional points warrant further comment. In order to determine reaction rates with CoLX<sub>2</sub><sup>+</sup> oxidants (X = Cl, Br, or NCS), reactions had to be run in a medium containing high [X<sup>-</sup>], partly owing to the relative lability of these complexes<sup>34c</sup> and partly owing to the extreme insolubility of the [CoLX<sub>2</sub>]ClO<sub>4</sub> salts. This probably does not present a serious complication for the Ru(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> reactions,<sup>9</sup> but does present an ambiguity in the case of the V<sup>2+</sup> reactions, since ligand exchange is relatively rapid on this reagent<sup>43</sup> and V<sup>2+</sup> reactions are often cat-

(43) For example, see reviews of significance of the intermediate

alyzed by  $[X^-]$ .<sup>42</sup> It also should be mentioned that much of our work with the chloro and bromo complexes was complicated by absorbance changes subsequent to the electron transfer reaction. At least some of this difficulty was traced to the extreme oxygen sensitivity of the cobalt(II) complexes in these systems and to the problem of rigorous isolation of reactant mixtures from air in the stopped-flow apparatuses. As a general rule, these complicating absorbance changes were considerably slower than the reactions of interest or could be eventually eliminated and do not present a serious problem in the interpretation of results.

The kinetic studies of  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions of *cis*- $\text{Co}(\text{en})_2\text{ClF}^{2+}$ , *cis*- $\text{Co}(\text{en})_2\text{OH}_2\text{F}^{2+}$ , and *trans*- $\text{Co}(\text{en})_2\text{F}_2^+$  are summarized in Table II.

**Table II.** Acid Dependence of the Reduction of Various Co(III) Complexes by  $\text{Ru}(\text{NH}_3)_6^{2+}$ <sup>a</sup>

Complex	$[\text{H}^+] \times 10^3 \text{ M}$	$k, \text{M}^{-1} \text{sec}^{-1}$ <sup>b</sup>	Medium
<i>cis</i> - $\text{Co}(\text{en})_2\text{ClF}^{2+}$	500.0	920	NaCl, HCl
	0.03	600	NaCl, HCl, Na acetate <sup>c</sup>
	500.0	1090	LiCl, HCl
	0.3	714	Li acetate, <sup>d</sup> HCl, LiCl
<i>cis</i> - $\text{Co}(\text{en})_2\text{FH}_2\text{O}^{2+}$	500.0	$3.35 \pm 0.35^e$	NaCl, HCl
	0.4	3.4	NaCl, HCl, Na acetate <sup>c</sup>
<i>trans</i> - $\text{Co}(\text{en})_2\text{F}_2^+$	0.5	0.57	Na acetate <sup>c</sup>
	0.05	0.78	Li acetate <sup>d</sup>
	90.0	1.00	NaCl, HCl
	200.0	1.24	NaCl, HCl
	300.0	1.35	NaCl, HCl
	450.0	2.02	NaCl, HCl

<sup>a</sup> 20°;  $\mu = 1.0 \text{ M}$ , except as indicated. <sup>b</sup> Errors in the rate constant resulting from a least-squares treatment of the second-order plots are  $\leq ca. 3\%$  of the tabulated values. Reproducibility of individual rate constants was better than 10%. <sup>c</sup> Sodium acetate, acetic acid buffer.  $\Sigma[\text{acetate}] = 0.045 \text{ M}$ . <sup>d</sup> Lithium acetate, acetic acid buffer, in a LiCl medium.  $\Sigma[\text{acetate}] = 0.045 \text{ M}$ . <sup>e</sup> Two determinations. Error limits are mean deviations.

In other work in progress in these laboratories,<sup>41</sup> we have observed that the presence of (TIM)cobalt(II) species catalyze the equilibration of  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$ . We have used this behavior, unusual among complexes of cobalt, to obtain a preliminary estimate of the self-exchange rate of  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+,2+}$ . In the first series of experiments, we determined the pH changes which occurred when  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{2+}$  was introduced (the concentrations were  $2.8 \times 10^{-4} \text{ M}$  in one experiment and  $5.2 \times 10^{-3} \text{ M}$  in another) into a solution of  $4 \times 10^{-4} \text{ M}$   $\text{Co}(\text{TIM})(\text{NH}_3)_2^{3+}$  initially at pH 3 (temperature = 25°,  $[\text{NaClO}_4] = 0.1 \text{ M}$ ). Then from the initial rate (*i.e.*,  $1/2 d[\text{NH}_4^+]/dt$ ) of reaction 4, we esti-



mate that  $k_4 = (1.7 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{sec}^{-1}$ . In control experiments, we found no significant changes in pH for at least 24 hr when  $\text{Co}(\text{TIM})(\text{NH}_3)_2^{3+}$  stood at pH 3 in the absence of  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{2+}$ . It is to be noted that our estimates of the potential for the respective cobalt(III)-cobalt(II) couples show that  $\Delta G^\circ = +(12 \pm 2) \text{ kcal/mol}$  in the electron-transfer step for (4) (*i.e.*,

lability of  $\text{V}^{2+}$  in (a) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968); (b) K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, **13**, 107 (1970).

neglecting protonation of  $\text{NH}_3$ ). In order to obtain an estimate of  $k_{\text{exch}}$  at  $\Delta G^\circ = 0$ , we have used Marcus' cross relation<sup>4,20</sup> and assumed that the self-exchange rates are not very different for  $\text{Co}(\text{TIM})(\text{NH}_3)_2^{3+,2+}$  and  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+,2+}$ .<sup>44,45</sup> The exchange rate so calculated is (at  $\mu = 1.0$ )  $\log k_{\text{exch}} = 2.8 \pm 0.8$ . This is probably a reasonable estimate of the outer-sphere exchange rate. For comparison, we have similar measures of the  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{2+}$  catalysis of the hydrolytic equilibration of  $\text{Co}(\text{TIM})\text{Cl}_2^+$ ; the inferred exchange rate (an upper limit) in this case is  $\sim 10^6 \text{ M}^{-1} \text{sec}^{-1}$ .

## Discussion

In this study we have been able to make reasonably reliable estimates of the standard free energy of reaction associated with the  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{V}^{2+}$  reductions of a variety of complexes of cobalt(III). As is noted below, these values of  $\Delta G_{12}^\circ$  parallel very closely the observed changes in reaction rates, thus confirming the suspicion raised several years ago when we compared our earlier rate measurements to estimated<sup>25</sup> changes in  $\Delta G_{12}^\circ$ . The resulting analysis of free energy relations and some related issues are treated in separate subsections below.

Since it was not possible to measure all the reaction rates at the same ionic strength, we have extrapolated all the specific rate constants (Table I) to unit ionic strength. This high ionic strength was selected for comparisons in order to minimize rate differences due only to electrostatic work terms. The extrapolation was made using eq 5<sup>47</sup> where  $Z_A$  and  $Z_B$  are the charge types

$$\log k = Z_A Z_B \text{fn}(\mu) \quad (5)$$

of the oxidant and reductant and  $\text{fn}(\mu)$  was determined from the experimental ionic strength dependence of several  $\text{Ru}(\text{NH}_3)_6^{2+}$ /cobalt(III) reactions.<sup>18,48,49</sup>

**A. Linear Free Energy Relations for Outer-Sphere Reductions of Cobalt(III) Complexes.** In Figure 2 we have plotted  $\log k_{12}$  vs.  $\Delta G_{12}^\circ$ <sup>48,50,51</sup> for every  $\text{Ru}(\text{NH}_3)_6^{2+}$  reduction of cobalt(III) for which we could find the appropriate data (except the  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  reactions). We have included data for  $\text{Co}(\text{NH}_3)_6^{3+}$  ( $E^\circ = +0.1 \text{ V}$ <sup>9,31</sup>) and  $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}$  ( $E^\circ$  estimated to be  $0.33 \text{ V}$ <sup>30</sup>) in this figure, both with measured rate constants<sup>9</sup> extrapolated to unit ionic strength. As we proceeded with this investigation, it soon became evident that the very simple correlation noted by Liteplo and Endicott<sup>13b</sup> was remarkably good. As a further test of the effectiveness of this simple proportionality between  $\log k_{12}$  and  $\Delta G_{12}^\circ$ , we have also investigated the reductions of  $\text{CoEDTA}^-$  and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$ . The data, with the exception of the  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  complexes (see below), agree well with the functional form of eq 1 but with little evidence for nonlinearity in the range  $0 \geq \Delta G_{12}^\circ \geq -18 \text{ cal/mol}$ .

(44) This latter assumption is consistent with some points raised in the discussion below and the observation that the self-exchange rates for  $\text{Co}(\text{NH}_3)_6^{3+,2+}$ <sup>48</sup> and  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{2+,2+}$ <sup>46</sup> are not much different.

(45) N. S. Birardar and D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 73 (1960).

(46) N. A. P. Kane-Maguire and J. F. Endicott, unpublished observations.

(47) J. W. Gryder, *J. Chem. Phys.*, **37**, 718 (1963).

(48) J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965).

(49) R. C. Patel, Ph.D. dissertation, Boston University, 1969.

(50) Values of  $\Delta G_{12}^\circ$  have been calculated from standard potentials<sup>30,31</sup> taking 0.1 V as the potential of the  $\text{Ru}(\text{NH}_3)_6^{3+,2+}$  couple.<sup>51</sup>

(51) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

It is convenient to express our experimental observations in the form  $-2.3RT \log k_{12} = a + b\Delta G_{12}^\circ$ . Then for  $\text{Ru}(\text{NH}_3)_6^{2+}$   $a = 1.7 \pm 0.4$  kcal/mol, and  $b = 0.58 \pm 0.07$ . The  $\text{V}^{2+}$  reactions are similar in their functional dependence on  $\Delta G_{12}^\circ$  (there is more scatter, particularly for reactions run at high  $[\text{X}^-]$ ) with  $a = 8 \pm 2$  kcal/mol and  $b = 0.56 \pm 0.08$ . It is significant that our experimental values of  $a$  are different by nearly the amount predicted (*i.e.*,  $-1.3/2 \log k_{\text{exch,Ru}} + 1.3/2 \log k_{\text{exch,V}} \approx 4$  kcal/mol while for  $\Delta G_{12}^\circ = 0$ ,  $a_{\text{Ru}} - a_{\text{V}} \approx -6 \pm 2$  kcal/mol)<sup>50-58</sup> for the  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{V}^{2+}$  reactions, while values of  $a$  apparently are not very sensitive to changes in the ligands coordinated to cobalt(III). It is particularly important to observe that when the reaction rates are properly corrected for their differing contributions to  $\Delta G_{12}^\circ$ , changes in axial ligands in a series of *trans*- $\text{Co}^{\text{III}}\text{LX}_2$  complexes do not result in very large changes in reaction rate. Since this conclusion holds for axial ligands varying from  $\text{NH}_3$  to  $\text{Br}^-$ , it would appear that the stretching of axial metal-ligand bonds<sup>2,1,53</sup> cannot contribute significantly to the observed activation energetics for cobalt(III) oxidants (see further comments about ligand stretching models below). For most cobalt(III) oxidants (the  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  complexes may differ in the details of their activation energetics; see below), the net free energy of reaction is the single most important factor determining the variation in the rate of reaction with a particular outer sphere<sup>54,57,58</sup> reductant.

Consideration of the reactions of  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+}$ ,  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{3+}$ ,  $\text{Co}(\text{EDTA})^-$ , and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  provides additional support for the conclusion of the preceding paragraph. It is to be noted that the four corresponding cobalt(III)-cobalt(II) couples have about the same reduction potential ( $0.57 \pm 0.03$  V), while the cobalt(III)-cobalt(II) self-exchange rates differ by a factor of more than  $10^{11}$  at  $25^\circ$ .<sup>40,59,60</sup> If

(52) In calculating the predicted correlation from  $\log k_{12} = 1/2(\log k_{11} + \log k_{22} + \log K_{12} + \log f_{12})$ , we have used  $k_{11} \approx 10^3 \text{ M}^{-1} \text{ sec}^{-1}$  or  $10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ , respectively, for the  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ <sup>53,54</sup> and  $\text{V}^{3+/2+}$  self-exchange rates. The latter is  $\sim$ one-tenth the self-exchange rate reported in the literature<sup>55</sup> and is based on the outer-sphere  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions. If the literature value were used the predicted  $\text{V}^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  rates would be nearly identical since the lower  $\text{V}^{3+/2+}$  self-exchange rate is almost exactly canceled by the more negative reduction potential.<sup>31,51</sup>

(53) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

(54) It might be observed that some authors, particularly Earley<sup>5d</sup> but also R. G. Linck (private communication), have recently questioned whether  $\text{Ru}(\text{NH}_3)_6^{2+}$  reactions are actually outer sphere. The questioning is appropriate, as no really direct evidence has been found. The work of Scheidiger, *et al.*,<sup>57</sup> cited by Earley<sup>5d</sup> as "evidence" for the possibility of inner-sphere association reflected on substitution in ruthenium(III), *not* ruthenium(II) complexes. Substitution for  $\text{NH}_3$  in  $\text{Ru}(\text{NH}_3)_6^{2+}$  is known to be slow,<sup>46</sup> but  $[\text{H}^+]$  catalyzed<sup>58</sup> (thus an acidic ligand might be able to function as a bridge in the activated complex in ruthenium(II) reductions). Even the oxidation of  $\text{Ru}(\text{NH}_3)_6^{2+}$  by  $\text{ClO}_4^-$  leaves the coordination sphere of the ruthenium intact<sup>46</sup> and need not involve expansion of the ruthenium coordination sphere.<sup>56</sup> We find the observed integrity of the  $\text{Ru}(\text{NH}_3)_6^{2+}$  coordination sphere<sup>9,46</sup> and relative unreactivity of hydroxy complexes of cobalt(III) the most persuasive evidence for the outer-sphere geometry.

(55) K. V. Krishnaumurti and A. C. Wahl, *J. Amer. Chem. Soc.*, **80**, 5921 (1958).

(56) G. Navon and D. Meyerstein, *J. Phys. Chem.*, **74**, 4067 (1970).

(57) J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 5928 (1968).

(58) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(59) These self-exchange rates are  $10^3 \text{ M}^{-1} \text{ sec}^{-1}$  at  $25^\circ$ ,  $\mu = 1.0$  (as estimated in this study);  $10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$  at  $70^\circ$ ,  $\mu = 1$ ;<sup>46</sup>  $5.8 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$  at  $70^\circ$ ;<sup>40</sup> and  $9 \times 10^{-7} \text{ M}^{-1} \text{ sec}^{-1}$  at  $25^\circ$ ,<sup>60</sup> respectively.

(60) F. S. Dainton, G. S. Laurence, W. Schneider, D. R. Stranks, and M. S. Vaidya, UNESCO Isotope Conference, Paris, 1957. Cited in ref 8b.

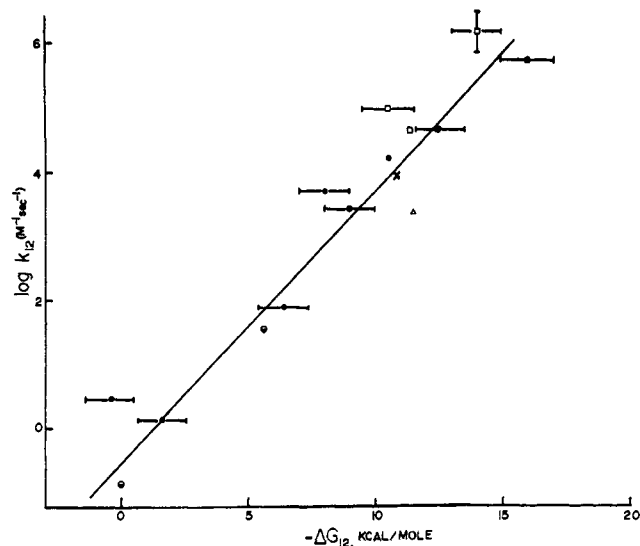


Figure 2. The dependence on the free energy of reaction ( $\Delta G_{12}^\circ$ ) of the second-order rate constant ( $k_{12}$ ) for  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions of various cobalt(III) complexes; estimated uncertainties of  $\Delta G^\circ$  are indicated for cases that  $E^0$  has been estimated from  $E_{1/2}$ : for  $\text{Co}(\text{trans}[14]\text{diene})\text{X}_2$  (●),  $\text{Co}(\text{teta})\text{X}_2$  (□),  $\text{Co}(\text{NH}_3)_5\text{X}^{3+}$  (X =  $\text{NH}_3$ ,  $\text{OH}_2$ ) (⊙),  $\text{Co}(\text{EDTA})^-$  (Δ), and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  (×).

(1) is used to determine  $\lambda_{\text{Co}}$  (*i.e.*,  $\lambda_{\text{Co}} \approx 4\Delta G_{\text{exch}}^\ddagger$ ) from the self-exchange rate data, and if<sup>61</sup>  $\lambda_{12} = 1/2(\lambda_{11} + \lambda_{\text{Co}})$ , then one would expect outer-sphere reduction specific rates to differ by a factor of more than  $10^5$  over this series of oxidants. Contrary to such expectation, the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions span a reactivity range of only about 200 and the  $\text{V}^{2+}$  reductions differ by a factor of only about 50. It is evident that the cross reactions do not depend on  $\lambda_{\text{Co}}$  nearly as strongly as predicted; *i.e.*, the simple additivity relation,<sup>61</sup>  $\lambda_{12} = 1/2(\lambda_{11} + \lambda_{\text{Co}})$ , proposed by Marcus is not applicable to the outer sphere reductions of cobalt(III). Thus the functional form 1 appears to be correct, but  $\lambda$  does not have the significance usually ascribed to it. There does appear to be a weak dependence of  $\log k_{12}$  on  $\lambda_{\text{Co}}$ , but the dependence on the reducing agent seems stronger than predicted by the Marcus correlation.<sup>52</sup>

(B) **Some Observations Concerning Specific Ligand Stretching Models.** The observations cited above suggest that most of the variations in reaction rate observed with different cobalt(III) oxidants arise from their differing contributions to  $\Delta G_{12}^\circ$ . For example, most of the greater reactivity in cross reactions of  $\text{CoLCl}_2^+$  compared to  $\text{CoL}(\text{NH}_3)_3^{3+}$  can be attributed to the fact that the former is a far better oxidant. This does not argue that the  $\text{Co}^{\text{III}}\text{-Cl}$  or  $\text{Co}^{\text{III}}\text{-NH}_3$  bonds are not stretched in the activated complex, but that such stretching makes a small contribution to the overall energetics of activation. Even with the systems we have reported in this paper, our knowledge of  $\Delta G_{12}^\circ$  is not sufficiently precise that we would be able to detect small deviations from (1) as for example would occur if  $\lambda_{12}$  varied a small amount from complex to complex. This problem is aggravated considerably by the apparently weak dependence of  $\Delta G_{12}^\ddagger$  on  $\lambda_{\text{Co}}$  discussed in the previous section. Thus, the specific rates of the  $\text{Ru}(\text{NH}_3)_6^{2+}$

(61) Recall that  $\lambda_{12}$  is the "intrinsic" reorganizational barrier for the cross reaction and  $\lambda_{11}$  and  $\lambda_{22}$  are the corresponding barriers for the two self-exchange reactions. For simplicity in the discussion, we have substituted  $\lambda_{\text{Co}}$  for  $\lambda_{22}$ .



reactions of  $\text{Co}^{\text{II}}(\text{NH}_3)_4\text{X}$  for  $\text{X} = \text{NH}_3, \text{H}_2\text{O}$ , and  $\text{Cl}^-$  parallel the variations in  $\Delta G_{12}^\circ$  one would expect in these systems,<sup>25,32</sup> while the reduction of  $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$  might seem anomalously slow.<sup>11</sup> By the same comparison, the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reduction of *trans*- $\text{Co}(\text{en})_2\text{F}_2^+$  also seems anomalously slow; however, estimates of the variations in potential based upon changes in crystal-field splittings are not reliable in every case.<sup>62</sup> In fact, we have found that  $\text{Co}(\text{en})_3^{3+}$  is reduced polarographically at potentials only  $\sim 0.2$  V more negative than that of *trans*- $\text{Co}(\text{en})_2\text{F}_2^+$ ,<sup>63</sup> suggesting that *trans*- $\text{Co}(\text{en})_2\text{F}_2^+$  is a very poor oxidant indeed and that the crystal-field model<sup>32</sup> incorrectly estimates the stability of fluoride (or hydroxide) complexes of cobalt(III) relative to cobalt(II). Certainly we must conclude that there is no evidence for as major a contribution to the reaction energetics from cobalt(III)-ligand stretching as was postulated by Patel and Endicott.<sup>11</sup>

**(C) Self-Exchange Rates and Related Problems.** Some comments seem to be in order regarding cobalt(III)-cobalt(II) self-exchange rates, even though aspects of these reactions are still under investigation in these laboratories. In principle, one could question whether the self-exchange reactions can be legitimately compared to the  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{V}^{2+}$  cross reactions, since there may be some mechanistic differences. Although we have no cause to doubt that the self-exchange for  $\text{Co}(\text{trans}[14\text{diene})(\text{OH}_2)_2]^{3+,2+}$ ,  $\text{Co}(\text{EDTA})^-$ , and  $\text{Co}(\text{C}_2\text{O}_4)_3^{3-}$  proceeds through an outer-sphere activated complex, the contrary assumption would require that the appropriate outer-sphere self-exchange rates are smaller than the literature values. Therefore, deviations from predicted behavior may be even greater than we have estimated above. On the other hand, it is to be observed that the  $\text{Co}(\text{TIM})(\text{NH}_3)_2^{3+}-\text{Co}(\text{TIM})(\text{OH}_2)_2^{2+}$  reaction is necessarily outer sphere. In estimating a self-exchange rate from this catalytic hydrolysis, we have assumed that the self-exchange rates of the diamino and diaquo complexes are the same. Thus, our estimated self-exchange rate may be too small and again deviations from theory may again be larger than estimated above. Furthermore, there is no  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+,2+}$  self-exchange rate which can be compatible with both the  $\text{V}^{2+}$  and  $\text{Ru}(\text{NH}_3)_6^{2+}$  reductions of  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+}$ . For these reasons, a more direct measure of the  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+,2+}$  self-exchange rate cannot change the qualitative significance of the preceding discussion. It is to be noted that the specific rates for the  $\text{Ru}(\text{NH}_3)_6^{2+}$  and  $\text{V}^{2+}$  reductions of  $\text{Co}(\text{TIM})(\text{NH}_3)_2^{3+}$  and  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+}$  are consistent with our treatment and the Marcus correlation (1).

It is most remarkable that present information indicates that some factors which are very significant in determining the self-exchange rates for cobalt(III)-cobalt(II) reactions do not make correspondingly great contributions to the outer-sphere reductions of the cobalt(III) complexes. At the same time, however, one must keep in mind that we observe a dependence of specific rate constant on  $\Delta G_{12}^\circ$  very close to that predicted by (1). There are probably several ways of

putting these observations together into a consistent theoretical model; however, we think that there are two ideas which deserve particularly close scrutiny. First of all, the weak dependence of the cross reactions on  $\lambda_{\text{Co}}$  may only imply that within the context of a Franck-Condon type model the reactant and product potential surfaces are coupled in the neighborhood of their crossing point in such a way that  $\lambda_{12} \neq \frac{1}{2}(\lambda_{11} + \lambda_{22})$ . The failure of the simple averaging of the individual reactant surfaces may be an important characteristic of cross reactions for those cases that  $\lambda_{\text{Co}} \gg \lambda_{11}$ .

The second mechanistic hypothesis of interest is that the cross and self-exchange reactions may differ in their spin multiplicity restrictions. For example, a restriction generally observed in triplet energy-transfer reactions is that spin multiplicity is conserved along the reaction coordinate.<sup>64,65</sup> The same condition applied to electron-transfer reactions of ruthenium(II) and cobalt(III) (both singlet ground states) would require that cobalt(II) be produced in a doublet state, since ruthenium(III) has a  $t_{2g}^5$  d-electronic configuration. In the great majority of cases the cobalt(III) self-exchange rates are determined for systems in which the ground electronic state of the six-coordinate cobalt(II) species is  $t_{2g}^5e_g^2$ ; therefore, the values of  $\lambda_{\text{Co}}$  determined from such exchange reactions could reflect constraints on the electronic transition probability which do not exist in the cross reactions. Similar considerations may not be applicable to the  $\text{V}^{2+}$ -cobalt(III) reactions, since the total spin moment of  $3/2$  may be achieved by adding a projection of  $t_{2g}^2$  to  $t_{2g}^5e_g^2$  as well as by a triplet-doublet combination of products.

The model described in the preceding paragraph suggests that the amazing  $\sim 10^{12}$  difference in the  $\text{Co}(\text{trans}[14\text{diene})(\text{OH}_2)_2]^{3+,2+}$  and  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+,2+}$  self-exchange rates might arise if the  $\text{Co}^{\text{II}}(\text{trans}[14\text{diene})\text{X}_2$  (X coordinated) complexes have the  $t_{2g}^5e_g^2$  electronic configuration, while the  $\text{Co}^{\text{II}}(\text{TIM})\text{X}_2$  complexes have the  $t_{2g}^6e_g$  ground-state configuration. The limited magnetic information<sup>29</sup> for the (*trans*[14diene)cobalt(II) complexes is not inconsistent with this hypothesis. No magnetic information is yet available for the  $\text{Co}^{\text{II}}(\text{TIM})\text{X}_2$  complexes. On the other hand, it is evident that in aqueous solution the equilibrium  $\text{Co}^{\text{II}}(\text{trans}[14\text{diene})\text{X}_2$  species are tetragonally distorted to the extent that  $\text{Co}^{\text{II}}-\text{X}$  interaction is not detectable and these complexes of cobalt(II) are low spin.<sup>29</sup> Thus, either spin constraints do not differ for the  $\text{Ru}(\text{NH}_3)_6^{2+}-\text{Co}(\text{trans}[14\text{diene})\text{X}_2$  and the  $\text{Co}-(\text{trans}[14\text{diene})(\text{OH}_2)_2]^{3+,2+}$  electron-transfer reactions or the spin changes in the latter are incredibly complex (since both reactants apparently have low-spin ground states). The weight of the limited information currently available would seem to argue that spin restrictions are not a major factor contributing to the peculiar reactivity patterns of cobalt(III) complexes. However, we are still investigating the self-exchange reactions and hope to contribute some more definite information on these points elsewhere. It may also be relevant that some authors have concluded that spin restrictions are not important in self-exchange reactions of bipyridyl, ter-

(62) J. J. Kim and P. A. Rock, *Inorg. Chem.*, **8**, 563 (1969).

(63) Both reductions show anodic voltammogram components. Although "irreversible" in the sense of peak breadth, these reductions are the most nearly reversible of any  $\text{Co}^{\text{II}}(\text{en})\text{X}_2$  systems we have investigated.

(64) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

(65) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970, Chapter 3.

pyridyl, and *o*-phenanthroline complexes of cobalt(III)-cobalt(II).<sup>66,67</sup>

## Conclusions

From information in the present study, it is clear that the predominant factor determining relative rates of reduction of most common cobalt(III) complexes by outer-sphere reductants is the variation in the free energy of reaction. The experimental data for such reactions can be represented by functions of the form  $\log k = a + b\Delta G^\circ + \dots$  for each reducing agent. The dependence on  $\Delta G^\circ$  is nearly that predicted by Marcus.<sup>4</sup> For the classical Werner-type complexes of cobalt(III), the experimental basis for determining the free energy of reaction is still lacking, but there is now a basis for making reasonable estimates; such estimates will be useful at least to the extent that they aid in identifying those systems which deviate significantly from such a simple pattern of free energy correlations. With the exception of  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  complexes, there are no significant deviations from the free energy correlation among the systems reported here; *i.e.*, most such deviations as we have observed fall within the error limits introduced by the imprecision of our knowledge of  $\Delta G^\circ$ , ionic strength extrapolations, etc. There are no doubt reactivity variations of the order of a factor of 2 or so in the rate constant which must be attributed to the "constant term,"  $a$ , in our correlations.

It has also been demonstrated in the present work with the  $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  complexes that there are cobalt(III) oxidants for which this constant term,  $a$ , does change markedly. In view of the large amount of speculation about axial ligand stretching models,<sup>5,11,21</sup> it seems appropriate that the first unambiguous example of a  $\Delta G^\circ$ -independent change in reactivity in cobalt(III) complexes should involve equatorial rather than axial ligands. The comparison of the *trans*-tetraamine complexes on the one hand with the corresponding *trans*- $\text{Co}^{\text{III}}(\text{TIM})\text{X}_2$  complexes on the other must provide us with one of the largest "nonbridging" ligand effects observed to date. Furthermore, the most startling contrast in reactivity among these systems is in the incredible range of self-exchange rates observed for *trans*- $\text{CoL}(\text{OH}_2)_2^{3+,2+}$  couples.

In reviewing the present study and other related studies of outer-sphere reductions of cobalt(III) complexes we can see no reason to doubt the basic validity of the Franck-Condon type models which have been proposed.<sup>4</sup> For example the predicted free energy dependence is indeed observed. However there are large failures of detail. The evidence of the present study suggests that the discrepancies between theory and experiment become progressively larger as the intrinsic reorganizational barriers ( $\lambda_{11}$  and  $\lambda_{22}$ ) of the oxidant and reductant become very different in magnitude (*e.g.*, for  $\lambda_{11} \gg \lambda_{22}$ ) at least for reactions involving cobalt(III). This suggests that there is either significant tunneling through Franck-Condon barriers or a failure of the theoretical models to properly couple the re-

actant and product potential energy surfaces in the neighborhood of their crossing point. In this regard, it is interesting to recall the observation<sup>12,18</sup> that the coefficients  $\alpha_X$  in eq 2 depend on the nature of the reducing agent oxidized by the  $\text{Co}^{\text{III}}(\text{en})_2\text{AX}$  complexes. In the cases that A is an amine (or  $\text{NH}_3$ ) and X is the same (*e.g.*,  $\text{X} = \text{Cl}$ ), we would predict that the various cobalt(III)-cobalt(II) reduction potentials are similar but not identical.<sup>68</sup> Thus one could attribute only very large variations in specific reaction rate with changes in A to differing contributions of  $\lambda$  terms to  $\Delta G_{12}^\ddagger$ . Only in the cases that A =  $\text{NH}_3$  or alkylamine is replaced by A = pyridine does the change in reactivity of  $\text{Co}^{\text{III}}(\text{en})_2\text{AX}$  complexes toward  $\text{Ru}(\text{NH}_3)_6^{2+}$  approximate the magnitude of the difference in reactivity exhibited by  $\text{Co}(\text{trans}[14]\text{diene})(\text{OH}_2)_2^{3+}$  and  $\text{Co}(\text{TIM})(\text{OH}_2)_2^{3+}$ . With this possible exception, most of the variations in reactivity toward  $\text{Ru}(\text{NH}_3)_6^{2+}$  of the  $\text{Co}^{\text{III}}(\text{en})_2\text{AX}$  complexes<sup>11</sup> probably arise from the contributions of the  $\Delta G_{12}^\circ$  terms in (1).<sup>68</sup> This conclusion is reinforced by the observation that the  $\text{Ru}(\text{NH}_3)_6^{2+}$  reactions do not depend strongly on  $\lambda_{\text{Co}}$ . Thus the conclusion reached above for reactions of cobalt(III), that  $\lambda_{12} \simeq 1/2(\lambda_{11} + \lambda_{22})$  only when  $\lambda_{11} \simeq \lambda_{22}$ , is consistent with the observation that  $\alpha_X(\text{Fe}) \simeq \alpha_X(\text{Ru})$  since  $\lambda_{\text{Ru}}$  and  $\lambda_{\text{Fe}}$  are similar in magnitude.<sup>4b,51,53</sup> Since  $\lambda_{\text{Cr}} > \lambda_{\text{V}} > \lambda_{\text{Fe}}$  and since one would expect for these systems that  $\lambda_{\text{Cr}} \sim \lambda_{\text{Co}}$ , contributions to  $\Delta G_{12}^\ddagger$  from  $\lambda_{\text{Co}}$  should decrease in relative significance, in the order  $\text{Cr} > \text{V} > \text{Fe} \geq \text{Ru}$ . As discussed elsewhere,<sup>11,13,18</sup> any detailed analysis of the  $\text{Cr}^{2+}$  reactions is necessarily complicated by contributions to the overall reaction energetics of steps associated with precursor complex formation and the transfer of the bridging ligand.

A final point which we wish to make is that the rates of outer-sphere and inner-sphere electron-transfer reactions ought to depend similarly on the free energy of reactions. This similarity in the functional dependence on  $\Delta G_{12}^\circ$  is no doubt the basis for the "success" of a correlation which we proposed in an earlier study.<sup>11</sup> However, a model of the activated complex<sup>11,20</sup> which we proposed at that time no longer seems very appropriate. Despite this expected similarity in their dependence on  $\Delta G_{12}^\circ$ , inner-sphere and outer-sphere reactions might generally be expected to differ in their intrinsic reorganizational barriers, and precursor complex formation (neglected in the earlier correlation) must make a contribution to the overall energetics of the inner-sphere reaction.<sup>10,13,18</sup> Thus the detailed free energy changes which can occur in the course of an inner-sphere electron-transfer reaction should be systematically and critically reexamined.

**Acknowledgments.** The authors are greatly appreciative of the generosity and useful discussions with Professor D. H. Busch and his collaborators about some of the complexes used in this study. We also appreciate the generosity of Professors T. Kimura and D. B. Rorabacher in making their stopped-flow apparatus available to us.

(68) Note that a difference of potential of only 0.1 V is expected to result in a sevenfold variation of the rate constant and that the change of potential of this magnitude is expected on replacement of ethylenediamine by two ammonia ligands.<sup>54</sup>

(66) R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968).

(67) J. K. Beattie and Sr. H. Elsbernd, Abstracts of Papers, presented at 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, INOR 25.