Oxidation–Reduction Chemistry of Complexes Containing Macrocyclic Ligands. Free-Energy Correlations for Oxidations of Cobalt(II) Complexes[1]

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Abstract: Rate constants for the outer-sphere oxidations of $Co^{II}(N_4)$, (N_4) = a tetradentate macrocyclic ligand, have been shown to be experimentally correlated to the standard free energy of reaction: $\Delta G^{\ddagger} = a + (0.33 \pm 0.07)\Delta G^{\circ} + \ldots$. Not only is this dependence on ΔG° much weaker than predicted, but the free-energy independent terms, a, which have been theoretically related to reorganizational energies, are not readily correlated to oxidant reorganizational parameters (as inferred from self-exchange rates). It is inferred that current theoretical models fail to consider some key factors which make major contributions to the reactivity patterns observed for cobalt complexes.

The experimental rates of many outer-sphere electron transfer reactions are in agreement with Marcus'[2] free-energy correlation (1).[2,3] A number of

$$\Delta G_{12}^{\ddagger} = \frac{\lambda_{12}}{4} + \frac{\Delta G^{\circ}_{12}}{2} + \frac{(\Delta G^{\circ}_{12})^2}{4\lambda_{12}} \qquad (1)$$

specific instances of failure of this relation have been noted,[4] and it has been a common, but not universal,[2e] opinion that the electron transfer reactions which are most generally not correlated by (1) are reductions of cobalt(III) complexes.[2,3] Even in these cases some limited success in the application of (1) has been achieved by treating the free-energy independent term of (1) as an adjustable parameter.[5] Until very recently, however, there have been few critical and systematic examinations of the applicability of correlations such as (1) to reactions of cobalt complexes.

We have recently made use of reversible and quasi-reversible potential data,[6–8] obtained in large part for cobalt complexes containing macrocyclic ligands, to establish that in empirical free-energy correlations (2)

$$\Delta G_{12}^{\ddagger} = a + b\Delta G^{\circ}_{12} + \ldots \qquad (2)$$

the coefficient b is 0.57 ± 0.08 for reductions of a large variety of cobalt(III) complexes by $Ru(NH_3)_6^{2+}$ and V^{2+}.[7–9] It is a conclusion of these studies that difficulties in applying (1) to electron transfer reactions of cobalt(III) arise mostly from the free-energy independent term. This conclusion has been strongly supported by studies of homogeneous[8,10] and heterogeneous[11] electron transfer rates among groups of complexes for which ΔG°_{12} = constant (or zero). This most recent work has demonstrated, for reductions of cobalt(III) complexes, that there is no simple linear relationship[3] between apparent reorganizational parameters of self-exchange and cross reactions. A possible inference is that electron transfer rates of cobalt(III) complexes are strongly influenced by some factors other than purely reorganizational (or Franck–Condon) factors. Since most of the macrocyclic complexes of cobalt(II), *i.e.*, the electron transfer products, are low spin the anomalous behavior observed cannot[12] be attributed to the kinetic effects of changes in spin multiplicity.[13,14]

In the present study we report our investigations of the applicability of (1) to the outer-sphere oxidations of two macrocyclic complexes of cobalt(II). The complexes in question, $Co(trans[14]diene)^{2+}$ and $Co(TIM)^{2+}$,[15,16] are stable (in the absence of strong oxidants), low-spin species in acidic aqueous solution, and are readily oxidized. Thus, in aqueous perchlorate media where the coordination environment of cobalt(II) is clear, these are better model systems for an assessment of the applicability of (1) than the cobalt(II) systems studied previously by Wilkins and coworkers.[17,18]

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[1] Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged.

[2] For pertinent reviews see: (a) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1966); (b) J. E. Earley, *Prog. Inorg. Chem.*, 13, 243 (1970); (c) R G. Linck, "MTP International Review of Science, Inorganic Chemistry," Ser. 1, Vol. 9, M. L. Tobe, Ed., University Park Press, Baltimore, Md., 1971; (d) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966; (e) N. Sutin, *Chem. Brit.*, **8**, 148 (1972).

[3] For the reorganizational parameters, λ_{12}, it is generally assumed that $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2 = 2\Delta G_{11}^{\ddagger} + 2\Delta G_{22}^{\ddagger}$; $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the free energies of activation observed in the self-exchange reaction of species 1 and 2, respectively. To simplify the discussion below we will use subscripts "12" to designate reductions of cobalt(III) and "21" to designate oxidations of cobalt(II).

[4] For example, see (a) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963); (b) J. F. Endicott and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1686 (1964).

[5] R. C. Patel and J. F. Endicott, *ibid.*, 90, 6364 (1968).

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

[7] M. P. Liteplo and J. F. Endicott, *ibid.*, **10**, 1420 (1971).

[8] D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Amer. Chem. Soc.*, **94**, 394 (1972).

[9] A least-squares analysis of data in Figure 2 of ref 8 ($Ru(NH_3)_6^{2+}$ reductions only and omitting points for $Co(EDTA)^-$ and $Co(C_2O_4)_3^{3-}$) gives a correlation, $\Delta G_{12}^{\ddagger} = (-1.0 \pm 0.5) + (0.64 + 0.05)\Delta G^{\circ}_{12}$. This correlation is further analyzed in the text below.

[10] D. P. Rillema and J. F. Endicott, *Inorg. Chem.*, 11, 2361 (1972).

[11] J. F. Endicott, R. R. Schroeder, and D. R. Ferrier, *J. Phys. Chem.*, submitted for publication.

[12] (a) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *Chem. Commun.*, 495 (1972).

[13] L. E. Orgel, *Rep. Solvay Conf. Chem., Brussels*, **10**, 329 (1956).

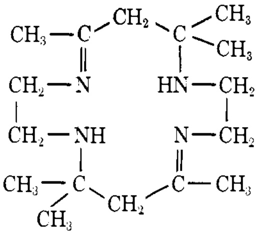
[14] H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).

[15] *trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene. In a recent paper, Busch, *et al.*, have suggested more useful abbreviations for these ligands: *trans*[14]diene = [14]dieneN_4 and TIM = [14]tetraeneN_4. See V. L. Goedkin, P. H. Merrell, and D. H. Busch, *J. Amer. Chem. Soc.*, **94**, 3397 (1972).

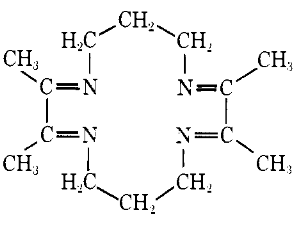
[16] The axial coordination positions in these cobalt(II) complexes are labile. Under our experimental conditions, aqueous perchlorate media, it will be assumed that these positions are occupied by solvent water.

[17] R. Farina and R. G. Wilkins, *Inorg. Chem.*, 7, 514 (1968).

[18] R. G. Wilkins and R. E. Yelin, *J. Amer. Chem. Soc.*, **92**, 1191 (1970).



trans[14]diene



TIM

Experimental Section

A. **Preparation of Compounds.** The complexes, $\mathrm{Co(phen)_3(ClO_4)_3 \cdot 2H_2O}$,[19] $\mathrm{Fe(bipy)_3(ClO_4)_3 \cdot 3H_2O}$,[20] $\mathrm{Na_3[Co(CO_3)_3] \cdot 3H_2O}$,[21] [Co(*trans*[14]diene)]$\mathrm{(ClO_4)_2 \cdot 2H_2O}$,[6] and $\mathrm{[Co(TIM)(OH_2)_2](ClO_4)_3 \cdot 2H_2O}$[8] were prepared as previously described. $\mathrm{[Fe(phen)_3](ClO_4)_2 \cdot H_2O}$, $\mathrm{[Fe(4,7\text{-}Me_2phen)_3](ClO_4)_3 \cdot 2H_2O}$, $\mathrm{[Fe(3,4,7,8\text{-}Me_4phen)_3](ClO_4)_3 \cdot 3H_2O}$ were prepared after the literature procedure.[20] $\mathrm{Co(NH_3)_5Br_3}$, $\mathrm{[Co(NH_3)_6](ClO_4)_3}$, $\mathrm{[Ru(bipy)_3](ClO_4)_3 \cdot H_2O}$, and [Co(*trans*[14]diene)$\mathrm{(OH_2)_2](ClO_4)_3}$ were available from prior studies in our laboratories.

$\mathrm{Co(TIM)(OH_2)_2(ClO_4)_2}$. A 0.67 g sample of $\mathrm{[Co(TIM)(OH_2)_2](ClO_4)_3 \cdot 2H_2O}$ was dissolved in 5 ml of 0.1 *M* $\mathrm{HClO_4}$ solution. The solution was deaerated prior to the addition of 6 ml of 0.2 *M* $\mathrm{Cr^{2+}}$ solution. The red product precipitated from the reactant solution. The precipitate was filtered, washed with methanol and then ether, and dried by aspiration. *Anal.* Calcd for $\mathrm{CoC_{14}H_{28}N_4O_{10}Cl_2}$: C, 31.00; H, 5.21; N, 10.33; Cl, 13.08. Found: C, 31.14; H, 5.21; N, 10.35; Cl, 12.99.

B. **Reactant Solutions.** Due to the large variety of reactive oxidants employed in this study the reaction conditions are outlined in some detail below.

(1) **Care and Handling of Oxidant Solutions.** (a) **$\mathrm{Fe(OH_2)_6^{3+}}$.** The source of hexaaquoiron(III) was the hydrated perchlorate salt (G. F. Smith). This was dissolved in 1 *M* perchloric acid to make a 0.1 *M* iron(III) stock solution. A determination of contamination by iron(II) was made using a stoichiometric threefold excess of 1,10-phenanthroline. There was less than 0.1% iron(II) in our stock solutions. Prior to reaction, the stock solution was diluted tenfold.

(b) **$\mathrm{Fe(bipy)_3^{3+}}$, $\mathrm{Co(TIM)(OH_2)_2^{3+}}$, Co(*trans*[14]diene)$\mathrm{(OH_2)_2^{3+}}$, and $\mathrm{Co(NH_3)_6^{3+}}$.** A 0.1 *M* $\mathrm{HClO_4}$ solution served as the medium for these oxidants. Due to the instability of the $\mathrm{Fe(bipy)_3^{3+}}$, stock solutions were used immediately after preparation and deaeration of the solution.

(c) **$\mathrm{[Co(NH_3)_5Br]Br_2}$.** $\mathrm{Co(NH_3)_5Br_3}$ was dissolved in an acidic perchlorate acid solution of pH 3. The ionic strength was adjusted to 0.1 *M* with $\mathrm{NaBF_4}$. The $\mathrm{NaBF_4}$ was recrystallized from water and dried under vacuum at 80° prior to use as an electrolyte.

(d) **$\mathrm{Ru(bipy)_3^{3+}}$.** To prepare stock solutions, sufficient solid $\mathrm{Na_3[Co(CO_3)_3] \cdot 3H_2O}$ was added to 1 *N* $\mathrm{H_2SO_4}$ solutions of $\mathrm{Ru(bipy)_3^{2+}}$ to oxidize about 50% of this complex to ruthenium(III). The $\mathrm{Ru(bipy)_3^{3+}}$ complex has been reported to be stable in solutions of pH ≤ 2.7.[20] Nevertheless, our best results were obtained when fresh solutions of $\mathrm{Ru(bipy)_3^{3+}}$ in 1 *N* $\mathrm{H_2SO_4}$ were used.

(e) **$\mathrm{Ce^{IV}}$.** Ceric ion was obtained from an acculute solution of ceric ammonium nitrate in 1 *N* $\mathrm{H_2SO_4}$.

(f) **$\mathrm{Fe(phen)_3^{3+}}$, $\mathrm{Fe(4,7\text{-}Me_2phen)_3^{3+}}$, and $\mathrm{Fe(3,4,7,8\text{-}Me_4phen)_3^{3+}}$.** The perchlorate salts of these complexes were very insoluble in most ionic media except 1 *N* $\mathrm{H_2SO_4}$. These complexes were found to be unstable in solution (except at high acidity) and consequently were used immediately after dissolving their perchlorate salts and deaerating the solutions.

(2) **Reductants.** Solutions of reductants were similar in pH and ionic strength to those of oxidants.

Solutions of $\mathrm{Co^{II}(EDTA)}$ were prepared *in situ* by addition of a stoichiometric quantity of $\mathrm{Na_2H_2EDTA}$ to the hydrate cobaltous perchlorate salt. The pH of the resulting solution was 4. At this pH, 97% of the complex is in the $\mathrm{Co^{II}EDTA}$ form.[7] The pH of the oxidant, $\mathrm{Fe(bipy)_3^{3+}}$, solution was also 4 and the ionic strength for both solutions was adjusted to 0.1 *M* with $\mathrm{NaClO_4}$. Since $\mathrm{Fe(bipy)_3^{3+}}$ is not very stable at pH >2.7,[20] oxidant solutions were used with an excess of $\mathrm{Co^{II}(EDTA)}$ immediately after preparation.

C. **Kinetic Procedures.** Reactions of Co(*trans*[14]diene)$\mathrm{(OH_2)_2^{3+}}$ with $\mathrm{Co(TIM)^{2+}}$ and $\mathrm{Co(TIM)(OH_2)_2^{3+}}$ with Co(*trans*[14]diene)$^{2+}$ were followed with a Cary 14 spectrophotometer at 545 nm (ϵ 3.45 × 10^3). Similarly, reactions of $\mathrm{Co(NH_3)_6^{3+}}$, $\mathrm{Co(phen)_3^{3+}}$, and $\mathrm{Co(NH_3)_5Br^{2+}}$ were monitored at the decrease in absorbance of the above reductants at 545 and 330 nm (ϵ 2.4 × 10^3), respectively. Reactions with $\mathrm{Fe(OH_2)_6^{3+}}$ and $\mathrm{Ce^{IV}}$ were followed in a similar manner except reactants were mixed with an Aminco stop flow apparatus.

The same device was used for the remaining reactions. The formation[22a] of $\mathrm{Fe(bipy)_3^{3+}}$ at 522 nm (ϵ 8650), $\mathrm{Fe(phen)_3^{2+}}$ at 510 nm (ϵ 11,100), $\mathrm{Fe(4,7\text{-}Me_2phen)_3^{2+}}$ at 510 nm, and $\mathrm{Fe(3,4,7,8\text{-}Mephen)_3^{2+}}$ at 500 nm (ϵ 13,800) were monitored for reduction of the corresponding iron(III) complexes by $\mathrm{Co(TIM)^{2+}}$, Co(*trans*[14]diene)$^{2+}$, and $\mathrm{Co^{II}(EDTA)}$.

The $\mathrm{Ru(bipy)_3^{3+}}$ oxidations of Co(*trans*[14]diene)$^{2+}$ and $\mathrm{Co(TIM)^{2+}}$ were followed at the $\mathrm{Ru(bipy)_3^{2+}}$ absorption[22b] maxima of 452 nm (ϵ 19,900) and 286 nm (ϵ 76,700), respectively.

All solutions were deaerated prior to mixing. A Tamsen constant-temperature bath was used for maintaining the reaction solutions and thermostated water jacketed spectrophotometric cell at 25°. Previously described[5] syringe techniques were used to mix reactants for the $\mathrm{Co(NH_3)_5Br^{2+}}$, Co(*trans*[14]diene)$\mathrm{(OH_2)_2^{3+}}$, $\mathrm{Co(phen)_3^{3+}}$, and $\mathrm{Co(TIM)(OH_2)_2^{3-}}$ reactions.

Most reactions were run under pseudo-first-order conditions with the reductant in greater than fivefold excess. Plots of log $|A - A_\infty|$ *vs.* *t* were linear up to five half-lives. At least three determinations were made of each rate constant.

In the case of the cerium(IV) reactions, [cerium(IV)] $\geq$ [cobalt(II)]. Since these reactions were sufficiently rapid that their observation approached the instrumental limitations, the cerium(IV) oxidations of $\mathrm{Co(TIM)^{2+}}$ were run both under pseudo-first-order and under second-order conditions of reactant concentrations. The second-order rate constants so obtained were in good agreement.

For reaction 3, ΔG° has been estimated to be -0.57 kcal/mol.[6-8]

$$\mathrm{Co}(trans[14]\mathrm{diene})\mathrm{(OH_2)_2^{3+}} + \mathrm{Co(TIM)^{2+}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Co}(trans[14]\mathrm{diene})^{2+} + \mathrm{Co(TIM)(OH)_2^{3+}} \quad (3)$$

By using a tenfold excess of Co(*trans*[14]diene)$\mathrm{(OH_2)_2^{3+}}$, k_3 was determined and was uncomplicated by the back reaction; similarly, a 25-fold excess of $\mathrm{Co(TIM)(OH_2)_2^{3+}}$ was used in determination of k_{-3}.

Results

Second-order rate constants for the oxidations of Co(*trans*[14]diene)$^{2+}$ and $\mathrm{Co(TIM)^{2+}}$ are collected in Table I. We have measured the rate of Co(*trans*[14]diene)$^{2+}$ oxidation with $\mathrm{Fe(bipy)_3^{3+}}$ in both 0.1 *M* perchloric acid and 1 *M* $\mathrm{H_2SO_4}$. The rates in both media were similar and suggest that direct comparisons may be made of the data obtained in 0.1 *M* perchloric acid and 1 *M* $\mathrm{H_2SO_4}$. Rates obtained in perchloric acid solutions of slightly higher ionic strength, 0.16 *M*, could be about twice as large as rates measured at 0.1 *M*, but would not change the general features of comparisons outlined below.

The sulfuric acid solution of cerium(IV) also contained nitrate ion. The oxidant capability of $\mathrm{NO_3^-}$ with Co(*trans*[14]diene)$^{2+}$ and $\mathrm{Co(TIM)^{2+}}$ was examined and we found that the reaction was very slow and therefore not a complication in analyzing the data.

The rate of $\mathrm{Co^{II}(EDTA)}$ with $\mathrm{Fe(bipy)_3^{3+}}$ was measured. It was $(6.8 \pm 0.1) \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$ at $\mu = 0.1$ *M* and $T = 25°$ in good agreement with Yelin and Wilkins.[18]

The thermodynamically unfavorable reactions of the macrocyclic cobalt(II) complexes with $\mathrm{Co(phen)_3^{3+}}$ and $\mathrm{Co(NH_3)_6^{3+}}$ were attempted. The reactions with

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[19] B. R. Baker, F. Basolo, and N. H. Newman, *J. Phys. Chem.*, **63**, 371 (1959).

[20] F. Burstall and R. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[21] H. F. Holtzclaw, Ed., *Inorg. Syn.*, **8**, 202 (1966).

[22] (a) R. R. Miller, W. W. Brandt, and Sr. M. Puke, *J. Amer. Chem. Soc.*, 77, 3179 (1955); (b) M. H. Ford-Smith and N. Sutin, *ibid.*, **83**, 1831 (1961).

Table I. Kinetic Parameters for Electron Transfer Reactions of Macrocyclic Complexes of Cobalt(II)

			$Co(TIM)^{2+}$			$Co(\textit{trans}[14]diene)^{2+}$		
Oxidant	$E°$, V[a]	k_{11},[b] M^{-1} sec^{-1}	Ionic strength	pH[c]	k_{12}, M^{-1} sec^{-1}	Ionic strength[c]	pH[c]	k_{12}, M^{-1} sec^{-1}
Ce^{IV}	1.44	4.6[g]	3.0[d]	0[d]	$(1.8 \pm 0.2) \times 10^6$	3.0[d]	0[d]	$(7.9 \pm 0.2) \times 10^5$
$Ru(bipy)_3^{3+}$	1.26	10^8 [h]	3.0[d]	0[d]	$(1.0 \pm 0.2) \times 10^7$	3.0[d]	0[d]	$(1.7 \pm 0.1) \times 10^6$
$Fe(bipy)_3^{3+}$	1.1	10^8 [h]	0.10	1.0	$(6.5 \pm 0.1) \times 10^5$	0.10	1.0	$(6.9 \pm 0.4) \times 10^4$
						3.0[d]	0[d]	$(6.0 \pm 0.4) \times 10^4$
$Fe(phen)_3^{3+}$	1.06	10^8 [h]	3.0[d]	0[d]	$(3.5 \pm 0.3) \times 10^5$	3.0[d]	0[d]	$(1.1 \pm 0.1) \times 10^5$
$Fe(Me_2phen)_3^{3+}$	0.88	19^8 [h]	3.0[d]	0	$(9.2 \pm 0.4) \times 10^4$	3.0[d]	0[d]	$(1.8 \pm 0.2) \times 10^4$
$Fe(Me_4phen)_3^{3+}$	0.85	10^8 [h]	3.0[d]	0[d]	$(4.1 \pm 0.3) \times 10^4$	3.0[d]	0[d]	$(3.2 \pm 0.1) \times 10^3$
$Fe(OH_2)_6^{3+}$	0.77	4.2[i]	0.16	1.0	$(1.0 \pm 0.1) \times 10^3$	0.16	1.0	$(1.5 \pm 0.1) \times 10^2$
$Co(\textit{trans}[14]diene)(OH_2)_2^{3+}$	0.56[k]	2×10^{-7} [e,f]	0.10	1.0	$(1.5 \pm 0.3) \times 10^{-3}$			
$Co(TIM)(OH_2)_2^{3+}$	0.54[k]	10^{2+1} [f]				0.10	1.0	$(6.1 \pm 0.1) \times 10^{-3}$
$Co(NH_3)_5Br^{2+}$	≈0.5[l]		0.10	3.0	$(1.3 \pm 0.1) \times 10^2$	0.10	3.0	(0.8 ± 0.1)
$Co(phen)_3^{3+}$	0.42	1.1[j]	3.0[d]	0[d]	$(1.8 \pm 0.1) \times 10^{-2}$			

[a] Standard reduction potential, from D. A. Buckingham and A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 6, except as indicated. [b] At 25° (in the medium indicated in this table), except as indicated. [c] Perchlorate ($NaClO_4$, $HClO_4$) except as indicated. [d] 1.0 *M* H_2SO_4. [e] At 70°. [f] μ = 1.0 *M*. [g] Reference 4a. [h] M. W. Dietrich and A. C. Wahl, *J. Chem. Phys.*, **38**, 1591 (1963). [i] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [j] B. R. Baker, F. Basolo, and A. M. Neumann, *ibid.*, **63**, 371 (1959). [k] Reference 8. [l] Estimated from $Co(NH_3)_6^{3+,2+}$; $E° = 0.1$ V + the potential difference obtained by substitution of Br^- for NH_3 in ref 6.

$Co(NH_3)_6^{3+}$ were too slow to obtain useful spectral changes; we would estimate $k \leq 10^{-3}$ M^{-1} sec^{-1} in this case.

Discussion

A. Qualitative Comparisons of Oxidations of Cobalt(II) Complexes. There have been few systematic mechanistic studies of the oxidations of cobalt(II) complexes.[2] Of these, the study most relevant to our work is the recent report by Adin and Espenson of oxidations of cob(II)aloxime.[23] Unfortunately these authors were concerned mostly with developing evidence for an inner-sphere reaction path, so really useful quantitative comparisons are not possible. Nonetheless the rates of reactions of various cobalt(II) complexes with $Co(NH_3)_5Br^{2+}$ may be usefully compared. For example the 160-fold faster rate of reduction with $Co(TIM)^{2+}$ than with $Co(\textit{trans}[14]diene)^{2+}$ is consistent with the general pattern that the former is the more facile reductant, presumably due to smaller ligand reorganizational barriers.[12] That the factors which contribute the large (approximately 10^9-fold) difference in self-exchange rates of the $Co(TIM)(OH_2)_2^{3+,2+}$ and $Co(\textit{trans}[14]diene)(OH_2)_2^{3+,2+}$ couples are not more manifest in the reductions of $Co(NH_3)_5Br^{2+}$ may merely be a reflection of the difference in energetics for inner-sphere and outer-sphere electron transfer paths (note that the reductions of $Co(NH_3)_5Br^{2+}$ are mechanistically ambiguous).

In contrast the cob(II)aloxime reduction of $Co(NH_3)_5Br^{2+}$ is reported to be 2.5×10^3 faster than the $Co(TIM)^{2+}$ reduction of the same complex under similar conditions. A good bit of this apparent difference in reactivity, no doubt more than a factor of 10,[24] must be due to the difference in reductant charge types (which should affect *both* the collision frequency and precursor complex lifetimes). Additionally we have been unable to reference the cob(II)aloxime reduction potential ($E_{1/2}$ = 0.32 V *vs.* sce in 60% H_2O, 40% methanol)[25] directly against our systems, so we would have to assume an uncertainty of ±0.1 V in any comparison involving standard reduction potentials (see discussion of free-energy correlations, below). Given these considerations we would infer that cob(II)aloxime is not extraordinarily more facile an electron transfer reductant than $Co(TIM)^{2+}$ or even $Co(\textit{trans}[14]diene)^{2+}$.

The rates of oxidations of ethylenediaminetetraacetate complexes of cobalt(II) reported by Wilkins and Yelin[18] parallel closely, both in magnitude and trend, the reactivity patterns analyzed in detail below.

B. Dependence of Reaction Rates on $\Delta G°$. In order to determine the dependence of the electron transfer rate constants k_{21} on $\Delta G°_{21}$,[3] we have used as oxidants the tris-1,10-phenanthroline and trisbipyridyl complexes of iron(III) and ruthenium(III). It is presumed that the self-exchange rates of these tris chelates are large and nearly diffusion controlled;[2,4a,26] thus the determination of the dependence of k_{21} on $\Delta G°_{21}$ is not expected to be complicated by large variations in $\Delta G^{\ddagger}_{11}$. Appropriate data are plotted in Figure 1. For oxidations of $Co(\textit{trans}[14]diene)^{2+}$ we find $\Delta G^{\ddagger}_{21} = (2.9 \pm 0.6) + (0.34 \pm 0.06)\Delta G°_{21}$[27] while for $Co(TIM)^{2+}$, $\Delta G^{\ddagger}_{21} = (4.1 \pm 0.5) + (0.32 \pm 0.04)\Delta G°_{21}$.[27] Clearly for oxidations of both of these cobalt(II) complexes, the dependence on $\Delta G°_{21}$ of the reaction rate constant is *significantly less* than theoretically predicted by (1) and significantly less than the experimentally determined dependence on $\Delta G°_{12}$ of the reduction rate constants for cobalt(III) complexes.[8] As noted above the limited data available indicate that the reactivity patterns of Co^{II}–EDTA complexes resemble strongly the behavior of our $Co(N_4)^{2+}$ complexes. This relatively weak dependence of k_{21} on $\Delta G°_{21}$ may be a general property of oxidations of cobalt(II) amine-type complexes, just as the much stronger[9] dependence of k_{12} on $\Delta G°_{12}$ appears to be a common feature of reductions of cobalt(III) amine-

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(23) A. Adin and J. H. Espenson, *Inorg. Chem.*, 11, 686 (1972).

(24) The factor would be about 15 for a critical separation of 6 Å at an ionic strength of 0.10 assuming a classical ionic strength correction to the outer-sphere precursor complex stability constant. For similar corrections to outer-sphere stability constants in substitution reactions see: R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(25) G. Costa, A. Puxeddu, and G. Tauzher, *Inorg. Nucl. Chem. Lett.*, 4, 319 (1968).

(26) D. Larsen and A. C. Wahl, *J. Chem. Phys.*, 53, 3765 (1965).

(27) Slopes and intercepts computed using linear least-squares program. Error limits are average standard deviations from the linear least-squares recursion fit of the data points.

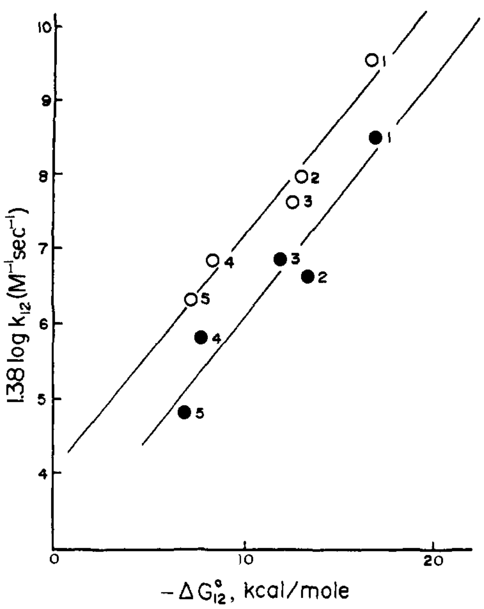

Figure 1. Free-energy dependence of cobalt(II) oxidations for similar oxidant reorganizational barriers. Reductants: ○, Co(TIM)$^{2+}$; ●, Co(*trans*[14]diene)$^{2+}$. Oxidants: 1, Ru(bipy)$_3{}^{3+}$; 2, Fe(bipy)$_3{}^{3+}$; 3, Fe(phen)$_3{}^{3+}$; 4, Fe(4,7-Me$_2$phen)$_3{}^{3+}$; 5, Fe(3,4,7,8-Me$_4$phen)$_3{}^{3+}$. For Co^{II}TIM, a = 4.1 ± 0.5, b = 0.32 ± 0.04; for Co^{II}(*trans*[14]diene), a = 2.9 ± 0.6, b = 0.34 ± 0.06.

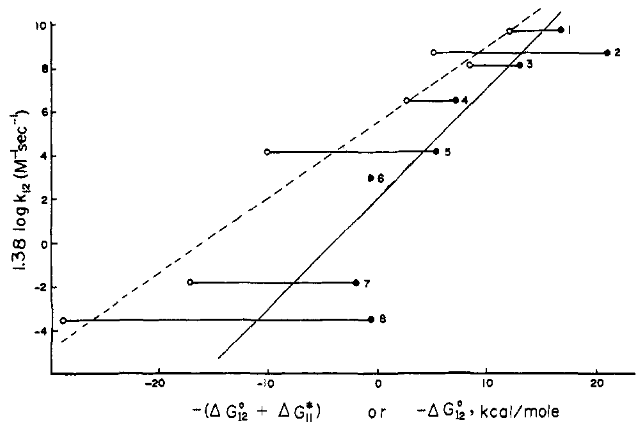

Figure 2. Free-energy dependence of Co(TIM)$^{2+}$ oxidations for variable oxidant reorganizational barriers. Oxidants: 1, Ru(bipy)$_3{}^{3+}$; 2, Ce^{IV}; 3, Fe(bipy)$_3{}^{3+}$; 4, Fe(3,4,7,8-Me$_4$phen)$_3{}^{3+}$; 5, Fe^{III}; 6, Co(NH$_3$)$_5$Br^{2+}; 7, Co(phen)$_3{}^{3+}$; 8, Co(*trans*[14]diene)(OH$_2$)$_2{}^{3+}$. The solid line is the theoretical slope and the dashed line is the observed behavior (defined in Figure 1): ●, $-\Delta G^{\circ}_{21}$; $\bigcirc_2$ $-(\Delta G^{\circ}_{21} - \Delta G^{\ddagger}_{11})$.

type complexes.[28,29] In fact it is to be observed that within our experimental error the experimental dependencies on ΔG° for oxidations of cobalt(II) and reductions of cobalt(III) are readily represented by equations of the type, $\Delta G^{\ddagger}_{21} = a_{21} + b\Delta G^{\circ}_{21}$ and $\Delta G^{\ddagger}_{12} = a_{12} + (1 - b)\Delta G^{\circ}_{12}$, respectively. The complementarity of the coefficients of ΔG° is consistent with the conventional requirement that the ratio of forward and reverse rate constants equal the equilibrium constant; however, the asymmetry of the dependence on ΔG° was unexpected.

The free-energy correlations discussed above are strictly empirical. In our studies to date[7-9] we have seen no evidence for a term second order in ΔG°. Although curvature has been observed, and accounted for using (1),[4] in free-energy correlations of electron transfer reactions, there is also good evidence that the second-order term in (1) does not make the predicted contribution for very negative values of ΔG°.[30] The *assumption* that (1) correctly describes the relationship between $\Delta G^{\ddagger}$ and ΔG°, and compensation for the second-order term, necessarily increases the apparent value of b in (2).[28,29] Thus application of such "corrections" would result in a_{21} = (3.2 ± 0.5) and b = (0.50 ± 0.05) for oxidations of Co^{II}(TIM) and a_{21} = (2.2 ± 0.6) and b = (0.45 ± 0.05) for oxidations of Co^{II}(*trans*[14]diene). Although this "correction" would indeed force our observations into agreement with (1), application of the same type of correction to the reductions of the corresponding cobalt(III) complexes[8] would result in a_{12} = (1.2 ± 0.7),[31] b = (0.70 ± 0.07)[31] compared to the "uncorrected" values of a_{12} = (1.0 ± 0.5) and b = (0.64 ± 0.05).[9] Thus it seems that simple expressions of the type (2) are more self-consistent than free-energy correlations which incorporate a second-order term based on (1), since: (a) there seems no logically consistent way to force both the oxidations of cobalt(II) complexes and the reductions of cobalt(III) complexes to agree with the predicted coefficient b = 0.5, and (b) the empirical correlations (2) give far better agreement with the expectation that b(Co(II)) = 1 − b(Co(III)). It must be emphasized that, within the limits of available experimental data, *the coefficients* correlating the free energy of reaction to the free energy of activation *depend more on the oxidation state of the cobalt* reactant than on variations in ligation[32] or, apparently, even of spin state of cobalt(II).

C. **Dependence of $\Delta G^{\ddagger}_{11}$.** The oxidants employed in this study exhibit a reasonably large variation (more than 10^{16}-fold) in their self-exchange rates. Since we have established the nature of the dependence of the rate constant on the free energy of reaction, it should be possible to establish a dependence of the cross reaction rate constant, k_{21}, on the self-exchange rate constant (or $\Delta G^{\ddagger}_{11}$) of the oxidant. This expectation has not been been realized. The nature of the difficulties encountered in attempted correlations are illustrated in Figure 2. If data for Fe^{3+} and cerium(IV) are omitted, the dashed line in Figure 2 would suggest for oxidations of Co(TIM)$^{2+}$ a correlation of the type

$$\Delta G^{\ddagger}_{12} = c_{21} + 0.3(\Delta G^{\circ}_{12} + \Delta G^{\ddagger}_{11})$$

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[28] Campion, Purdie, and Sutin[29] have reported a relatively weak (b = 0.27) empirical dependence of $\Delta G^{\ddagger}_{12}$ on ΔG°_{12} for the Co^{3+} oxidations of trisphenanthroline complexes of iron(II). As these authors further note, correction of $\Delta G^{\ddagger}_{12}$ for the dependence on $(\Delta G^{\circ}_{12})^2$ predicted by (1) would result in the expected slope.

[29] R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 3, 1091 (1964).

[30] For example, see: D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970).

[31] The precise values of a_{12} and b depend somewhat on the self-exchange rate constants which are used. For Co(*trans*)[14]diene)X$_2$ complexes the cobalt(III)-(II) self-exchange rate constants are extremely sensitive to X, varying from a minimum value of perhaps 10^{-9} M^{-1} sec^{-1} for X = H$_2$O to values of the order of 10^6 M^{-1} sec^{-1} for X = Cl and Br.[12] With various assumptions about the appropriate values of self-exchange rate constants we have been able to vary b from (0.69 ± 0.05) to (0.74 ± 0.06). The assumptions in the latter case are probably the most experimentally justifiable. It is to be observed that we have performed these "corrections" for a term in $(\Delta G^{\circ})^2$ for the sake of argument and at the prompting of Dr. Norman Sutin; it is not our intention to imply that this "correction" has any physical significance.

[32] Observe that b is apparently 0.27 for Co(OH$_2$)$_3{}^{3+}$ [29] in contrast to the value of 0.64 for *trans*-Co^{III}(*trans*[14]diene)X$_2$.

This is clearly inconsistent with the usual expectation;[2–4] furthermore no simple such free-energy correlation adequately encompasses all our observations. Although the factors which determine the magnitudes of self-exchange rates (k_{11}) may contribute weakly to cross-reaction reactivity patterns, the functional relationships are not clear at this time and in fact some additional factors must enter into the cross-reaction reactivity patterns.

D. Dependence of $\Delta G^{\ddagger}_{22}$. In reductions of cobalt(III) complexes it has been observed that the reorganizational parameters, λ_{Co}, inferred from cobalt(III)–(II) self-exchange rates often do not contribute appreciably to the free-energy independent term of (2) in cross reactions.[8,10,11] If we use the relative reactivities of Co(TIM)$^{2+}$ and Co(*trans*[14]diene)$^{2+}$ as a probe of this behavior, then it is clear that oxidations of these two complexes differ in their rates by more than a factor of about 10 only when the oxidant is a cobalt(III) complex! Clearly the factors which contribute to the large ($>10^8$) difference in the self-exchange rates of these two complexes make only a relatively minor contribution to these cross-reaction reactivity patterns. In fact the relative rates of oxidation of the Co(*trans*[14]diene)$^{2+}$ and Co^{II}–EDTA complexes are "too fast" by a factor of from 10^2 to 10^5. This is extremely similar to the behavior observed for reductions of cobalt(III) complexes.[8,10,11,29]

Conclusions. We have found that for oxidations of several cobalt(II) complexes, $\Delta G^{\ddagger}_{21} = a_{21} + 0.33\Delta G^{\circ}_{21}$. The free-energy independent term, a_{21}, is not a strong function of the activation free energies of the self-exchange reactions of *either* oxidant or reductant. These observations differ only in some details from the implications of related studies of reductions of cobalt(III) complexes.[8,10,11,29] Although the observed asymmetry of the free-energy dependence of cobalt(III) reductions compared to cobalt(II) oxidations might be rationalized in terms of potential energy surfaces which are asymmetric in the neighborhood of the transition state, such rationalizations do not readily accommodate the inferred very weak dependence on λ_{Co} of both oxidations of cobalt(II) and reductions of cobalt(III). We must therefore conclude that if the magnitudes of the rate constants for self-exchange reactions are determined only by Franck–Condon reorganizational parameters, then some other factors must make appreciable, perhaps dominant, contributions to the magnitudes of the rate constants observed in the cross reactions of, at least, cobalt complexes.

At this point it should be observed that a traditional interpretation[33] of our observed dependencies on ΔG° of the oxidations of cobalt(II) and reductions of cobalt(III) would be that the cobalt center in the activated complex for cross reactions more strongly resembles cobalt(II) than cobalt(III). In terms of ligand reorganizational energies, this suggests that before the electron is transferred there is more stretching of bonds at cobalt(III) than there is compression of metal ligand bonds at cobalt(II). Continuing this line of reasoning one would infer that variations in λ_{Co}, as deduced from cobalt(III)–(II) self-exchange reactions and which do not greatly affect cross-reaction reactivities, should be attributed mostly to variations in the work required to compress the cobalt(II) ligand bonds in order to achieve similar nuclear configurations around the cobalt(II) and cobalt(III) centers in the self-exchange reactions. The only available X-ray crystallographic evidence suggests that such changes in nuclear configuration are too small to account for observed variations in self-exchange reactivities, at least for Co(NH$_3$)$_6$$^{3+,2+}$.[14] More importantly, this inference would require that the contributions of λ_{Co} and ΔG° be strongly coupled in cross reactions, contrary to observation.[34] Thus we conclude that, even if there are significant differences in the cobalt(II) reorganizational energies in cross and self-exchange reactions, there must be yet another factor which contributes significantly to observed reactivity patterns.

One possible additional factor, contributing to both cross-reaction and self-exchange rates, might be derived from considerations of the variations in donor and acceptor orbital overlap with the electronic structure of the reactant metallo complexes. Thus in Marcus' treatment it is assumed that the transmission coefficient $\kappa \cong 1$,[35,36] while the overlap integral $\int \phi_D \phi_A d\tau$ does not make an appreciable contribution to the reaction energetics. An alternative assumption might be that $\kappa \cong 1$ only if $\int \phi_D \phi_A d\tau$ is greater than some minimum value, γ, which is not necessarily of large magnitude. In octahedral transition metal complexes, donor and acceptor orbitals have either $t_{2g}(\pi)$ or $e_g(\sigma)$ symmetry with respect to the metal ligand bonding axes. Since electron density in t_{2g} and e_g orbitals must be differently disposed with respect to the ligands, the condition $\int \phi_D \phi_A d\tau \geq \gamma$ will require different activated complex geometries and different critical distances of reactant separation in cases of t_{2g}–t_{2g}, e_g–e_g, and t_{2g}–e_g overlap. It is not appropriate to assume that work required to achieve the $\int \phi_D \phi_A d\tau \geq \gamma$ condition in t_{2g}–e_g overlap case is any kind of simple average of the corresponding work terms for the t_{2g}–t_{2g} and e_g–e_g cases.

It is also to be observed that cross relation proposed recently by Rosseinsky,[37] *i.e.*, $k_{12} = k_{11}{}^{\alpha}k_{22}{}^{1-\alpha}K_{12}{}^{\alpha}$, is inappropriate as it requires a much stronger dependence of k_{12} on self-exchange rate constants than is experimentally observed.

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(33) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963.

(34) Note that if the ΔG° dependence is removed from the cross-reaction reactivity patterns, then the contributions of λ_{Co} to $\Delta G^{\ddagger}_{12}$ vary with the nature of the reducing agent,[10] while $\Delta G^{\ddagger}_{21}$ is not very sensitive to either λ_{Co} or $\lambda_{oxidant}$, provided the oxidant is not a cobalt(III) complex.

(35) As Sutin[29,36] has pointed out if some of the cobalt self-exchange reactions are nonadiabatic and the cross reactions are adiabatic, then $\kappa_{12} \cong 1$ while $\kappa_{22} \ll 1$, so that the intercepts of free-energy correlation (2) would be too large while the depencence on ΔG° would be about as predicted. This is consistent with some, but not all experimental observations as noted above; however, if we set aside questions of whether (1) correctly predicts the relationship between $\Delta G^{\ddagger}$ and ΔG°, then the point raised cannot be easily refuted. In fact, if we use Sutin's notation[36] and set $k = pZe^{-\Delta G^{*}/RT}$ then the major formal difference between Sutin's argument and ours would be that we do not associate p with κ and that we allow p to be temperature dependent (a contribution from other than reorganizational, ΔG^{*}, work terms). We have developed the argument outlined here because it has some intuitive appeal and because as far as we can determine from available data (*e.g.*, see ref 10) differences in reactivity are more often associated with differences in the experimental $\Delta H^{\ddagger}$ than with the $\Delta S^{\ddagger}$ term.

(36) (a) N. Sutin, *Accounts Chem. Res.*, 1, 225 (1968); (b) private communication to J. F. E.

(37) D. R. Rosseinsky, *Chem. Commun.*, 225 (1972).