(13) C. S. Springer, D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).
(14) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972); 339 (1973).
(15) R. E. Cramer and R. Dubois, *J. Am. Chem. Soc.*, **95**, 3801 (1973); A. M. Grotens, J. J. M. Backus, F. W. Pijpers, and E. de Boer, *Tetrahedron Lett.*, 1467 (1973).
(16) J. H. Frosberg, *Coord. Chem. Rev.*, **10**, 195 (1973).
(17) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
(18) J. P. Fackler, *Adv. Chem. Ser.*, **No. 62**, 580 (1967).
(19) Assuming that slow exchange is ineffective in averaging the different environments of these methyl resonances.
(20) A possible reason for the absence of 2:1 adduct formation is that, on forming a 1:1 adduct, the delocalized electron density of the β-diketone chelate ring is drawn toward the attached Eu(fod)$_3$. Hence the Lewis basicity of the three oxygens at the opposite end of the Co(acac)$_3$ molecule would be lowered such that their tendency to coordinate to a second Eu(fod)$_3$ is reduced.
(21) In all cases duplicate runs using nondeuterated Eu(fod)$_3$ were made and the results obtained substantiate those obtained with Eu(fod-d_9)$_3$. Similarly a duplicate set of spectral studies using C$_6$D$_6$ as solvent were carried out for each of the systems discussed. In each case the C$_6$D$_6$ spectra were in qualitative agreement with the analogous spectra using CDCl$_3$ as solvent.
(22) The amount of benzene was in each case calculated from the elemental analysis and was also obtained from accurate integration of the NMR spectra of the adduct dissolved in CDCl$_3$. The benzene is strongly held since it is not removed by heating the compounds at 100 °C in vacuo for 12 h. It is not uncommon for clathrated solvent molecules to be held strongly in the host metal complex structure; see L. F. Lindoy, S. E. Livingstone, T. N. Lockyer, and N. C. Stephenson, *Aust. J. Chem.*, **19**, 1165 (1966).
(23) The wide-scan spectrum also confirms that no additional adduct signals fall outside the −10 to +10 ppm scanned in the previous study.
(24) L. F. Lindoy, H. C. Lip, H. W. Louie, M. G. B. Drew, and M. J. Hudson, *J. Chem. Soc., Chem. Commun.*, 778 (1977).
(25) The structure of these binuclear adducts is of considerable intrinsic interest since related examples in which all bridging oxygens are derived from acetylacetone ligands occupying the coordination sphere of a single metal ion appear to be quite rare.
(26) D. G. Buckley, G. H. Green, E. Ritchie, and W. C. Taylor, *Chem. Ind. (London)*, 298 (1971); R. von Ammon, R. D. Fischer, and B. Kanellakopulos, *Chem. Ber.*, **104**, 1072 (1971); W. D. Perry and R. S. Drago, *J. Am. Chem.*

Soc., **93**, 2183 (1971); H. N. Cheung and H. S. Gutowsky, *ibid.*, **94**, 5505 (1972); R. D. Bennett and R. E. Schuster, *Tetrahedron Lett.*, 673 (1972).
(27) Although a T^{-1} dependence has been predicted theoretically, the dependence may in fact be more complicated than this; see W. DeW. Horrocks, J. P. Sipe, and D. Sudnick in ref 2, p 33; R. M. Golding and P. Pyykko, *Mol. Phys.*, **26**, 1389 (1973); E. W. Stout and H. S. Gutowsky, *J. Magn. Reson.*, **24**, 389 (1976).
(28) It is noted that the halogen-substituted complexes nevertheless show the reverse order to that expected from the relative electronegativities of the substituent halogens. The electronic effects discussed should largely contribute to the enthalpy term for each equilibrium. Since related entropic considerations are far less predictable, these could be the source of the minor irregularity observed for the chloro- and bromo-containing adducts. Alternatively the variation may arise from subtle effects arising from different steric properties of the complexes.
(29) F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970).
(30) D. R. Eaton and K. Zaw, *Can. J. Chem.*, **49**, 3315 (1971).
(31) K. C. Williams and T. L. Brown, *J. Am. Chem. Soc.*, **88**, 4234 (1966); L. M. Seitz and T. L. Brown, *ibid.*, **88**, 4140 (1966).
(32) Nevertheless an alternate mechanism involving substrate displacement by solvent attack, such as

$$LS + solvent \rightarrow solvent\text{-}LS \rightarrow solvent\text{-}L + S,$$

cannot be ruled out. Further, it is not possible to distinguish a dissociative mechanism involving a lowering of coordination number of the europium(III) or one in which the coordination number is maintained by substituting solvent molecules.
(33) A related series of preliminary studies involving Pr(fod-d_9)$_3$ has also been performed. In the investigation of Co(β-diketonato)$_3$ complexes with Pr(fod-d_9)$_3$, slow chemical exchange was again observed as indicated by the presence of both adduct and free substrate NMR signals. Similar experiments to those carried out for the Eu(fod)$_3$ systems confirmed that 1:1 adduct formation occurred. As expected for Pr(fod)$_3$, the directions of the lanthanide-induced shifts are opposite in sign to those obtained for the europium LSR. Preliminary experiments concerned with deciding the nature of the slow exchange mechanism indicated that the details are more complicated than for Eu(fod)$_3$ exchange and no detailed analysis was attempted.
(34) For this adduct, a saturation point is reached at −40 °C after which no change in line width is observed. The reason for this behavior is uncertain.

Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Halide-Mediated Electron Transfer Involving Low-Spin Cobalt(III)–(II) Couples[1]

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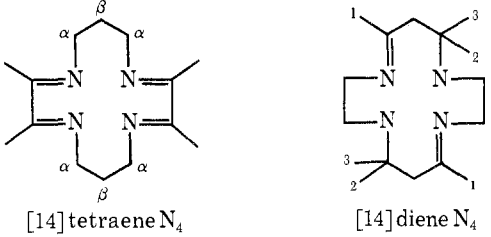
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Abstract: Coordination complex oxidants containing coordinated chloride and bromide react with low-spin Co^{II}(N$_4$)(OH$_2$)$_2$$^{2+}$ substrates (N$_4$ a tetraaza macrocyclic ligand) at rates about 10^6 times faster than with reagents constrained to react through outer-sphere pathways. Chloride transfer has been demonstrated in "exchange-like" reactions with Co(N$_4$)(OH$_2$)Cl^{2+} oxidants. As expected of rate patterns for systems exhibiting weak coupling between metal centers, the halide-bridged inner-sphere reactions vary in their rates over several orders of magnitude. The rate constants are dependent on the free energy of reaction and on intrinsic reorganizational parameters. A series of reactions of the type Co(N$_4$)(OH$_2$)Cl^{2+} + Co(N$_4$')(OH$_2$)$_2$$^{2+}$ $\rightleftarrows$ Co(N$_4$)(OH$_2$)$_2$$^{2+}$ + Co(N$_4$')(OH$_2$)Cl^{2+} has been investigated in which the low-spin cobalt(II) complexes are known to differ in their axial, Co–OH$_2$ bond lengths, and for which this structural difference is known to be directly reflected in a several orders of magnitude range of outer-sphere Co(N$_4$)(OH$_2$)$_2$$^{3+,2+}$ electron transfer rate constants. With reference to this series of reactions the 10^6-fold rate advantage of the Cl$^-$-bridged inner-sphere pathway has been shown to arise from (1) a much smaller reorganizational term associated with first coordination sphere bond length changes (50% of λ_i for the outer-sphere pathway); (2) a reduction of the solvent reorganizational term (λ_o) to nearly zero; and (3) possibly a small contribution (of the order of a factor of 30 in the rate constant) due to the greater adiabaticity of the inner-sphere reactions. For sufficiently powerful oxidants, the inner-sphere rates approach a limiting value, one or two orders of magnitude smaller than the diffusional limit, consistent with rate-determining substitution on the low-spin Co(N$_4$)(OH$_2$)$_2$$^{2+}$ complex ($k_w \sim 10^9$ s^{-1}).

Introduction

At the present stage of maturity in the study of electron transfer reactions there is general agreement on many of the gross features which determine patterns of reactivity.[2] However, the limits of theoretical descriptions have not always been well substantiated by experimental evidence, and in some kinds of system it is not clear what kind of theoretical model is applicable. Thus those electron transfer reactions in which a

Table I. Summary of ^{1}H NMR Spectra of Co(N$_4$)XY Complexes

[14]tetraeneN$_4$　　　　　　　[14]dieneN$_4$

complex	δ_{CH_3}	δ_α	δ_β
Co([14]tetra-eneN$_4$)(OH$_2$)$_2$$^{3+}$	3.19	2.64 t	4.45 m
Co([14]tetra-eneN$_4$)-(OH$_2$)Cl^{2+}	3.01	2.58	4.31

complex	δ_{CH_3}^{1}	δ_{CH_3}^{2}	δ_{CH_3}^{3}
Co([14]-dieneN$_4$)-(OH$_2$)$_2$$^{3+}$	2.99 s	1.89 s	1.27 s
Co([14]-dieneN$_4$)-(OH$_2$)Cl^{2+}	2.86 s	1.82 s	1.27 s

single halide ligand bridges the reactant centers at the moment of electron transfer have been very difficult to approach from a theoretical point of view owing to ambiguity about the strength of electronic coupling of metal centers by the bridging ligand. Numerous studies have indicated that halide bridging ligands greatly facilitate electron transfer between σ^*-donor and σ^*-acceptor complexes; however, the critical evaluation of reorganizational parameters in such studies has not been possible owing to lack of knowledge of the driving force of the reactions studied and of critical self-exchange parameters. Indeed, the fact that the inner-sphere pathway predominates in some systems might lead one to suspect that the coupling could be so strong that Franck–Condon-type activation barriers predicted on the basis of weak interaction models[3,4] should be washed out. Yet the existence of simple linear free energy correlations[2a,c,5-8] between inner-sphere and outer-sphere reductions of complexes of the types Co(NH$_3$)$_5$X^{2+} and Co(en)$_2$AX^{2+} strongly suggests that similar factors affect the rates of both categories of electron-transfer reactions.

In the limit of "weak" interaction between donor and acceptor metal centers, and for reactions with small driving forces (i.e., for $|\Delta G_{12}°| < \lambda_{12}$, where $\Delta G_{12}°$ is the standard free energy change for the reaction conditions and λ_{12} is Marcus' intrinsic reorganizational parameter; see eq 1), the rates of a large number of electron-transfer reactions are determined by the work required (1) to bring the reactants together (coulombic work terms); (2) to expand or contract reactant coordination shells in order to achieve the nuclear configurations appropriate to the transition state (inner-sphere reorganizational energy, λ_i); and (3) for the repolarization of the solvent from an environment appropriate for the precursor complex to the environment appropriate to a transition state (outer-sphere reorganizational energy, λ_o). For outer-sphere reactions, this more or less classical limit results in the simple free-energy correlation[2-4,9]

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

A closely related treatment of inner-sphere reactions has resulted in simple correlations of optical and thermal electronic transitions.[4b,c]

Cobalt(II) complexes containing 14-membered macrocyclic (N$_4$) ligands are thermally stable low-spin species in aqueous

solution.[10] These species are axially distorted, with the odd electron in an orbital which is largely d$_{z^2}$ in character.[10] Consequently electron exchange between these species and their cobalt(III) analogues involves transfer of an electron between metal σ^* orbitals. Since donor and acceptor orbitals in these systems are shielded from direct overlap by the axial ligands, while an appropriate ligand bridging the metals could mix donor and acceptor (σ^*) orbitals, electron transfer in these systems should exhibit a strong sensitivity to bridging ligand effects. The axial lability of the Co^{II}(N$_4$)X$_2$[10,11] complexes and the relative inertness of the Co^{III}(N$_4$)X$_2$[11,12] complexes is the classical combination which permits examination of bridging ligand effects.[2,13] Owing to their different axial Co^{II}-OH$_2$ bond lengths[10,14] the *trans*-Co([14]dieneN$_4$)(OH$_2$)$_2$$^{3+,2+}$ (ΔCo-OH$_2$ = 0.57 Å) and *trans*-Co([14]tetraeneN$_4$)-(OH$_2$)$_2$$^{3+,2+}$ [15] (ΔCo-OH$_2$ = 0.38 Å) have different inner-sphere reorganizational barriers, λ_i(OS), and this difference is directly reflected in the respective outer-sphere self-exchange rate constants (3×10^{-5} and 6×10^{-2} M^{-1} s^{-1}).[16] We have used these and related couples as probes of the intrinsic barriers, λ(I.S.), in halide-mediated, inner-sphere electron-transfer reactions.

Experimental Section

Preparation and Characterization of Complexes. The synthesis and characterization of most of the macrocyclic complexes used in this study have been described in detail elsewhere.[10,12,16-21] The compounds used in this study had absorption spectra and elemental compositions in agreement[16] with the previous reports.

The aquo–chloro complexes, Co(N$_4$)(OH$_2$)Cl^{2+}, used in this study are relatively difficult to isolate and purify. Of these species, Co([14]dieneN$_4$)(OH$_2$)Cl^{2+} [18f] and Co([14]tetraeneN$_4$)(OH$_2$)-Cl^{2+} [22] have been previously isolated and characterized. To prepare the Co(N$_4$)(OH$_2$)Cl^{2+} complexes for this study we dissolved approximately 1 g of [Co(N$_4$)Cl$_2$]ClO$_4$ in 0.001 M HClO$_4$ and warmed the solution to 45–50 °C for 15 min. The resulting solution was then passed through a Bio-Rad AG1-X8 anion exchange resin in the ClO$_4$$^-$ form. Absorption spectra are reported in Table S-1,[23] ^{1}H NMR spectra in Table I.

The reagents [Co(NH$_3$)$_5$Br]Br$_2$,[24] Na[Co(edta)],[25] and Na-[Co(edtaH)Cl][26] were prepared according to procedures described in *Inorganic Synthesis*. The preparation of [Ru(NH$_3$)$_5$py](ClO$_4$)$_2$ has been described by Ford et al.[27] The K$_3$IrCl$_6$ and K$_2$IrCl$_6$ were purchased from Alfa Inorganics. The [Co(NH$_3$)$_5$Cl]Cl$_2$ was available from previous studies in this laboratory and was recrystallized from 1 M HCl.

[14]dieneN$_4$　　　　　　　[14]tetraeneN$_4$

[14]dieneN$_4$-one　　　　　[14]py-dieneN$_4$
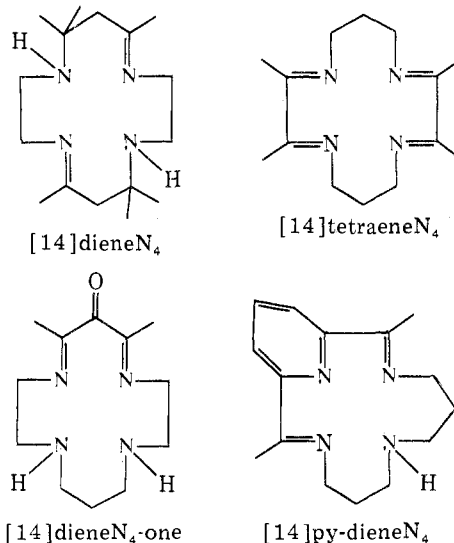
Warning. The heavy metal perchlorate salts prepared for this study can be detonated and are potentially hazardous.

Solutions and Techniques. The Co^{3+} [28] and Mn^{3+} [29] solutions were prepared by electrolysis of solutions of Co(ClO$_4$)$_2$·6H$_2$O and Mn(ClO$_4$)$_2$·6H$_2$O, respectively, in 3.0 M HClO$_4$ at 0 °C on a plati-

num gauze electrode. To generate Co^{3+} solutions, a 0.01 M Co^{2+} solution in 3 M $HClO_4$ was electrolyzed in a cooled electrolysis cell for about 6 h; the average current through the cell was 140 mA. Solutions of Mn^{3+} were generated from 0.2 M Mn^{2+} by electrolysis in the cooled cell for 15 min at 20 mA. All concentrations of Mn^{3+} and Co^{3+} in reagent solutions were determined by adding excess Fe^{2+} and determining the $[Fe^{3+}]$ spectrophotometrically as the SCN^- complex. The Fe^{2+} solutions were passed through a Jones reductor and all analytical determinations were referenced to appropriate blanks. Under our analytical conditions ($\sim$2.5 × 10^{-3} M Fe^{2+}, $\sim$0.25 M NaSCN, $\sim$0.5 M $HClO_4$) the absorptivity of the iron(III)–thiocyanate complex was determined to be ϵ 8270 ± 250 M^{-1} cm^{-1} at 480 nm, with respect to oxidation of Fe^{2+} by standardized Ce^{4+} solutions. Stock solution concentrations determined in this manner were in good agreement with direct determinations of Co^{3+} and Mn^{3+} using ϵ 35 M^{-1} cm^{-1} at 605 nm[28] and 78 M^{-1} cm^{-1} at 470 nm,[29] respectively.

The reagent Cr^{2+} solutions used in this work were produced by zinc amalgam reduction of 0.2 or 0.5 M Cr^{2+} in 1 M $HClO_4$.

Water used for reagent solutions was either redistilled over alkaline permanganate in an all-glass apparatus or passed through a Corning demineralizing column and distilled in an all-glass Corning "Mega-Pure" still.

The kinetic techniques employed were variations of those employed and described previously, as noted below. For reactions with 4 h > $t_{1/2}$ < 1 min, reactions were monitored using a Cary 14[6,18] spectrophotometer. Thermostated, deaerated solutions were transferred by means of a syringe to serum-capped spectrophotometer cells. Deaeration was accomplished by entraining stock solutions, cells, etc., with a stream of Cr^{2+}-purged argon.
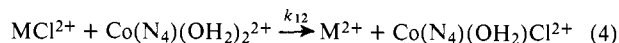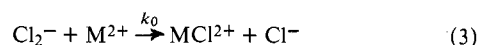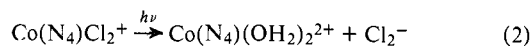
The $Co(NH_5)_5Cl^{2+}$ oxidations of $Co([14]dieneN_4)(OH_2)_2^{2+}$ were sufficiently sluggish that we had to use a freeze–thaw method of deaeration and an apparatus with the reaction cell isolated from the atmosphere by means of stopcocks. Blank determinations without added oxidant indicated that oxidation by O_2 (due to leaks) did not interfere with this system or with the $Co(NH_5)_5Cl^{2+}$ oxidation of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$.

NMR spectra were determined in a Varian T-60 spectrometer. Significant features of these spectra are reported in Table I for key complexes. In general we have found the $Co(N_4)OH_2X^{2+}$ NMR peaks to be broadened in the presence of $Co(N_4)(OH_2)_2^{2+}$. The extent of the line broadening was found to be proportional to $[Co(N_4)(OH_2)_2^{2+}]$: plots of the corrected line width vs. $[Co(N_4)(OH_2)_2^{2+}]$ were approximately linear. We have used the slope of such a plot to determine the $Co([14]tetraeneN_4)(OH_2)Cl^{2+}/Co([14]tetraeneN_4)(OH_2)_2^{2+}$ self-exchange rate ($k_{exch} = \Delta\nu/\pi$).[30] Corrections for variations in field homogeneity, sample paramagnetism, etc., have been made with respect to variations in the line width of a standard sample of tetramethylammonium perchlorate or acetone contained in a concentric insert. The deaerated sample solutions were 0.1 M in CF_3SO_3H.

Stopped-flow studies were performed using a thermostated Aminco apparatus.[18a–c] For reactions in solutions containing cobalt(II) complexes and large concentrations of halide ($[X^-] > 0.1$ M), the mixing chamber, driving syringes, etc., of the Aminco apparatus were fitted with a glovebag which was purged with Cr^{2+}-scrubbed Ar or N_2.

Flash photolysis studies were performed using standard techniques and Xenon Corp. apparatus described previously.[31,32] Deaerated solutions were transferred to the quartz, jacketed sample cell under N_2 in an all-glass system.

The half-lives of $CoCl^{2+}$ and $MnCl^{2+}$ in 1.0 M HCl are on the order of a few seconds.[33] In order to use these species as oxidants it was therefore necessary to generate them in the reaction solutions. The following scheme was utilized for the generation and subsequent reactions of MCl^{2+} with $Co(N_4)(OH_2)_2^{2+}$. The first reaction (2) has already been well characterized[31] and proceeds with a reasonable yield (typically $\sim$1 × 10^{-6} M of Cl_2^- for the flash system used). Reaction 3 has also been thoroughly studied for cobalt[34] but not for manganese.

$$Co(N_4)Cl_2^+ \xrightarrow{h\nu} Co(N_4)(OH_2)_2^{2+} + Cl_2^- \tag{2}$$

$$Cl_2^- + M^{2+} \xrightarrow{k_0} MCl^{2+} + Cl^- \tag{3}$$

$$MCl^{2+} + Co(N_4)(OH_2)_2^{2+} \xrightarrow{k_{12}} M^{2+} + Co(N_4)(OH_2)Cl^{2+} \tag{4}$$

In order to evaluate the rate constants, k_{12}, for reactions 4 we set $[MCl^{2+}]_{t=0} = [Co(N_4)(OH_2)_2^{2+}]_{t=0}$ (at t = 0 for reaction 4). The absorptivities of the $Co(N_4)Cl_2^+$ complexes preclude any significant contributions due to (5) when the cobalt(III) complexes are present. Changes in concentration were determined by monitoring the intense charge transfer to ligand absorbancies of the cobalt(II) complexes. The second-order plots were always linear to at least 2 half-lives.

The reaction of $IrCl_6^{2-}$ with $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ was followed by both flash-photolysis and stopped-flow techniques. The flash-photolysis experiments were carried out owing to the difficulty of measuring very fast reactions, such as this one, with the stopped-flow apparatus which is limited by a 4-ms mixing time.

The reaction

$$IrCl_6^{3-} \xrightarrow{h\nu} IrCl_6^{2-} + e^- \tag{5}$$
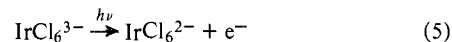
was used to generate $IrCl_6^{2-}$,[35] and when this species was generated in the presence of added $Co(N_4)(OH_2)_2^{2+}$, it decayed principally by the reaction

$$Co([14]tetraeneN_4)(OH_2)_2^{2+} + IrCl_6^{2-} \rightarrow$$
$$Co([14]tetraeneN_4)(OH_2)_2^{3+} + IrCl_6^{3-} \tag{6}$$
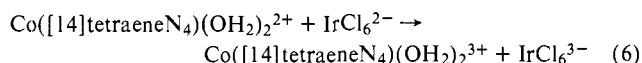
(reactions 9 and 10 describe the fate of the remaining radicals). The concentration of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ was in excess so that reaction 6 would be pseudo first order. Under these conditions, the transient decay obeyed first-order kinetics and was linearly dependent on the concentration of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$. A small increase in absorbance at 542 nm prior to the expected bleaching was attributed to the $IrCl_6^{2-}$ which has a λ_{max} at 490 nm, ϵ 3660,[35] and therefore should also absorb at 542 nm. Similar decay rate constants were determined from absorbance changes at 490 and 542 nm. The results of the flash photolysis and stopped-flow determinations are in reasonable agreement considering that the latter instrument had to be pressed to its limits and that the stopped-flow determinations had to be carried out under second-order conditions.
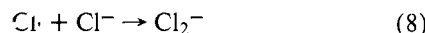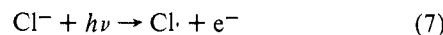
Reactions were run under pseudo-first-order conditions whenever possible. Activation parameters were calculated from a least-squares fit of a plot of log k/T vs. $1/T$. Errors were estimated using standard statistical techniques (68% confidence limits).[36]

Results

A. Oxidations of the $Co(N_4)(OH_2)_2^{2+}$ Substrates.

Most of the reactions studied were reasonably well behaved and the results are presented in Table II. The reactions of edta complexes presented special problems and will be treated in a separate section.

The flash-photolysis technique has been employed in this study as a very convenient means for the in situ generation of the powerful oxidants $CoCl^{2+}$, $MnCl^{2+}$, and $IrCl_6^{2-}$. Of these $MnCl^{2+}$ has not been previously reported.

A long-lived transient is generated by means of reaction 3 for both manganese and cobalt when the Cl_2^- radical is generated in the absence of $Co(N_4)(OH_2)_2^{2+}$ species. Thus when solutions containing M^{2+} in 1 M HCl are irradiated, reactions 3 and 7–10 occur.

$$Cl^- + h\nu \rightarrow Cl\cdot + e^- \tag{7}$$

$$Cl\cdot + Cl^- \rightarrow Cl_2^- \tag{8}$$

$$e^- + H^+ \rightarrow H\cdot \tag{9}$$

$$2H\cdot \rightarrow H_2 \tag{10}$$

We found the previously unreported $MnCl^{2+}$ species to have an absorption maximum at 290 nm. This is plausible for the charge transfer to metal transition in this complex since λ_{max} occurs at 270 nm for $CoCl^{2+}$ [34] and 340 nm for $FeCl^{2+}$ [33] so that the transition energies parallel the reduction potentials of M^{3+}.[28,29,37,38] The half-life for decay of $MnCl^{2+}$ in 1 M HCl under our conditions ($\sim$10^{-2} M Mn^{2+}) was approximately 30 s. Under the same conditions ($\sim$10^{-2} M Co^{2+}) the transient half-life of $CoCl^{2+}$ was about 5 s. This is in qualitative agreement with the reported decay of $CoCl^{2+}$, which is a complex function of $[Co^{2+}]$, $[Cl^-]$, and $[H^+]$.[34]

Table II. Kinetic Parameters for Selected Electron Transfer Reactions

oxidant	range of 10^4 [oxidant]^a	temp, °C	k, M^{-1} s^{-1} ^{b}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} deg^{-1}
A. Oxidations of Co([14]tetraeneN$_4$)(OH$_2$)$_2{}^{2+}$ ^{c}					
Co(NH$_3$)$_5$Br^{2+}	7.9–13	10	115 ± 4		
	6.3–13.5	24	247 ± 6		
	7.6–14.3	35	360 ± 40	31 ± 3	−96 ± 33
Co(NH$_3$)$_5$Cl^{2+}	0.64–1.0	24	22 ± 2^d		
Co^{3+}	2.2–5.8	25	337 ± 23^e		
Mn^{3+}	0.9–4.7	25	(1.7 ± 0.2) × 10^5 ^{e}		
CoCl^{2+}	~10^{-2}	25	(1.5 ± 0.1) × 10^7 ^{d,f}		
MnCl^{2+}	~10^{-2}	25	(2.4 ± 0.6) × 10^7 ^{d,f}		
IrCl$_6{}^{2-}$	~10^{-2} ^{g}	25	(2.9 ± 0.4) × 10^6 ^{d,f}		
IrCl$_6{}^{2-}$	0.08–0.16	25	(5.2 ± 0.5) × 10^6 ^{h}		
B. Oxidations of Co([14]dieneN$_4$)(OH$_2$)$_2{}^{2+}$ ^{i}					
Co(NH$_3$)$_5$Br^{2+}	19–25	16	0.40 ± 0.04		
	20–24	25	0.69 ± 0.01		
	18–23	35	1.1 ± 0.1	36 ± 3	−125 ± 25
Co(NH$_3$)$_5$Cl^{2+}	19–27	25	0.042 ± 0.003		
Co^{3+}	4.7–10	25	66 ± 2^e		
Mn^{3+}	1.7–4.7	25	(1.7 ± 0.1) × 10^4 ^{e}		
CoCl^{2+}	~10^{-2}	25	(1.6 ± 0.2) × 10^6 ^{f,g}		
MnCl^{2+}	~10^{-2}	25	(5.3 ± 0.2) × 10^6 ^{f,g}		
C. Oxidations of Ru(NH$_3$)$_5$py^{2+}					
Co(NH$_3$)$_5$Br^{2+}	5.9–12	10	9 ± 1		
	5.6–12	24	20 ± 1		
	5.8–12	35	29 ± 3	33 ± 4	−109 ± 38
Co([14]tetraeneN$_4$)Cl$_2{}^+$	4.1–10.3	10	(2.5 ± 0.3) × 10^5 ^{j}		
	1.9–10.5	24	(2.9 ± 0.6) × 10^5 ^{j}		
	2.6–5.9	35	(3.6 ± 0.2) × 10^5 ^{j}	8 ± 2	−113 ± 25
Co([14]dieneN$_4$)Cl$_2{}^+$	4.0–9.2	10	(8.0 ± 0.3) × 10^3 ^{j}		
	5.0–10.2	24	(1.2 ± 0.1) × 10^4 ^{j}		
	4.8–9.7	35	(1.7 ± 0.1) × 10^4 ^{j}	19 ± 3	−105 ± 25
Co([14]tetraeneN$_4$)(OH$_2$)$_2{}^{3+}$	6.3–9.1	10	(6.8 ± 0.9) × 10^3 ^{k}		
	5.0–15.2	25	(8.3 ± 0.9) × 10^3 ^{k}		
	5.1–8.2	35	(8.5 ± 0.5) × 10^3 ^{k}	4 ± 6	−155 ± 63
Co([14]dieneN$_4$)(OH$_2$)$_2{}^{3+}$	5.5–11	10	19 ± 3^k		
	6.5–8.3	25	36 ± 2^k		
	4.8–8.0	35	56 ± 4^k	29 ± 3	−117 ± 17
Co(NH$_3$)$_5$Cl^{2+}	7.4–11.7	24	3.9 ± 0.5		
Co(edtaH)Cl$^-$	1–2.4	24	(6.2 ± 0.3) × 10^4 ^{j}		
Co([14]tetraeneN$_4$)Br$_2{}^+$	2.5–3.1	24	(9.1 ± 0.2) × 10^4 ^{l}		
Co([14]dieneN$_4$)Br$_2{}^+$	4.2–7.1	24	(1.0 ± 0.1) × 10^5 ^{l}		

^{a} Excess reagent except as noted. ^{b} 0.1 M NaClO$_4$, pH 2, except as indicated. ^{c} Reactions monitored at 540 nm, ϵ[Co^{II}(N$_4$)] 3250 M^{-1} cm^{-1}. ^{d} 1 M HCl. ^{e} 3 M HClO$_4$. ^{f} From flash photolysis; see text. Average and average deviation of two to four determinations. ^{g} [Co([14]tetraeneN$_4$)(OH$_2$)$_2{}^{2+}$] = (0.13–2.0) × 10^{-5} M. ^{h} [HCl] = 0.5 M, [HClO$_4$] = 0.5 M, 25 °C, stopped-flow determinations, [Co([14]tetraeneN$_4$)(OH$_2$)$_2{}^{2+}$] = 5.1 × 10^{-6} M. ^{i} Reactions monitored at 340 nm, ϵ[Co^{II}(N$_4$)] 2500 M^{-1} cm^{-1}, except as noted. ^{j} 0.1 M NaCl, pH 2. ^{k} 0.1 M HClO$_4$. ^{l} 0.1 M NaBr, pH 2.

B. Reactions of Co(edta)$^-$ and Co(edtaH)Cl$^-$ with Co(N$_4$)-(OH$_2$)$_2{}^{2+}$. The reactions of both Co(edta)$^-$ and Co(edtaH)Cl$^-$ with two of the macrocyclic cobalt(II) complexes have been investigated. The results of these studies are reported in this section. The interpretation of the results, however, is complicated by the pH dependence of the rate law.

In the range of hydrogen-ion concentration 0.1–1 M the rate of reduction of Co(edtaH)Cl$^-$ by Co(N$_4$)(OH$_2$)$_2{}^{2+}$ increases with increasing [H$^+$]. Similar behavior has been observed for reduction of Co(edtaH)Cl$^-$ by Fe^{2+}.[39,40] The second-order rate constants were reported[38,39] to vary according to the equation log k(obsd) = log k_0 + A[H$^+$], where A = 0.12 over the range [H$^+$] = 0.05–0.7 M. The reaction has been shown to proceed via a chloride-bridged transition state by Haim and Sutin.[41]

The value of A we estimate for the reaction with Co([14]-tetraeneN$_4$)(OH$_2$)$_2{}^{2+}$ was 0.43, much larger than those reported by Ohashi et al.[40] The pH dependence, however, was observed *only* when the Co(edtaH)Cl$^-$ was dissolved in the solution containing the LiCl or NaCl *and* HCl prior to the reaction. If the Co(edtaH)Cl$^-$ was dissolved in water and then

mixed with a solution of the macrocyclic complex in the appropriate medium no hydrogen-ion dependence was observed. It is evident that the side reaction of Co(edtaH)Cl$^-$ at high [H$^+$] is much slower than the reaction with the macrocyclic complex. The reaction of Co(edtaH)Cl$^-$ with the medium must involve more than simple electrostatic association of H$^+$ or Na$^+$,[42] which would be diffusion controlled. Substitution of Cl$^-$ by H$_2$O can also be ruled out because that reaction is known to be very slow (k = 2 × 10^{-3} min^{-1} at 45 °C[38]). No data are available, however, on the substitution at a carboxylic acid site and this seems to be a very reasonable alternative explanation to Higginson's; it certainly accounts for our observations.

The reactions of Co(edta)$^-$ are very slow and show an even more complex hydrogen-ion dependence. This oxidant is in equilibrium with several other species in solution dependent on [H$^+$]. In the range [H$^+$] = 0.1–1 M the dominant species are probably Co(edta)(OH$_2$) and Co(edta)$^-$. The equilibrium constant has been determined:[39]

$$K_a = 1.28 \text{ M}^{-1} = \frac{[\text{Co(edtaH)(OH}_2)]}{[\text{H}^+][\text{Co(edta)}^-]}$$

The redox reactions carried out with $[H^+] < 1$ do not follow simple second-order kinetics. The pseudo-first-order kinetic plots suggest that the reactions involve an approach to an equilibrium which is pH dependent. The reaction is very slow at pH 2 and the equilibrium appears to be very much on the reactant side. One explanation for this behavior is that these reactions are reversible. The extent of reaction would then be dependent on the stability of the cobalt(II) product, which is known to decrease with increasing hydrogen ion concentration. The reactions with $Co(edtaH)(OH_2)$ or $Co(edta)^-$ also seem to be complicated by problems similar to those encountered with $Co(edtaH)Cl^-$. Using the initial rates a very crude estimate of the value of A may be calculated. For the range $[H^+] = 1-0.1$ M, $A \sim 0.54$. Our data can be fitted to a linear relation of $k(obsd)$ and $[H^+]$ as well as to the exponential relation proposed by previous workers.[38,39]

Our observations on these systems are summarized in Table III.

C. Oxidation of $Ru(NH_3)_5py^{2+}$. A variety of at least potentially inner sphere oxidants have been reacted with $Ru(NH_3)_5py^{2+}$. The data are consistent with the second-order rate law expected for a simple electron transfer reaction. The ionic strength was 0.1 at pH 2 for all these measurements. These reactions were run under pseudo-first-order conditions with the oxidant in excess. In several cases we used NaX media to maintain $Co(N_4)X_2^+$ as the predominant oxidant species.[12] The results of these determinations are summarized in Table II.

D. $Co(N_4)(OH_2)_2^{2+}$-Catalyzed Hydrolyses of $Co(N_4)X_2^+$. The $Co([14]dieneN_4)X_2^+$ complexes (X = Cl, Br) were dissolved in deaerated methanol. A 0.3-mL aliquot of this solution was transferred by means of a syringe to a spectrophotometer cell containing 3 mL of 0.1 M $HClO_4$ and various concentrations of $Co([14]dieneN_4)(OH_2)_2^{2+}$ and the reactions were followed at the charge transfer maxima ($\epsilon(273$ nm) 1.5×10^4 M^{-1} cm^{-1} for X = Cl and $\epsilon(274$ nm) 1.9×10^4 M^{-1} cm^{-1} for X = Br).[18d]

The $Co([14]tetraeneN_4)(OH_2)_2^{2+}$-catalyzed hydrolyses of $Co([14]tetraeneN_4)X_2^+$ were investigated using stopped-flow techniques and a dilution technique described previously.[12] A deaerated 0.1 M NaX solution containing $Co([14]tetraeneN_4)X_2^+$ at pH 2 was mixed with a deaerated 0.1 M $HClO_4$ solution containing the $Co([14]tetraeneN_4)(OH_2)_2^{2+}$. These reactions were monitored at the halide to metal charge transfer bands, 264 nm (ϵ 1.6×10^4 M^{-1} cm^{-1}) for X = Cl and 302 nm (ϵ 2.0×10^4 M^{-1} cm^{-1}) for X = Br. Spectroscopic changes were consistent with those reported previously for the first hydrolyses of these complexes.[12,18d]

For both families of complexes the observed hydrolysis rate constant (k_h) was linearly dependent on $[Co(N_4)(OH_2)_2^{2+}]$: $k_h = k_{h,0} + k_{Co}[Co(N_4)OH_2)_2^{2+}]$. The results of these studies are summarized in Table IV and the kinetic data may be found in Table SII.[23]

E. $Co(N_4)(OH_2)Cl^{2+}/Co(N_4)(OH_2)_2^{2+}$ Reactions. We have investigated the reactions

$$Co(N_4)(OH_2)Cl^{2+} + Co(N_4')(OH_2)_2^{2+}$$

$$\underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} Co(N_4)(OH_2)_2^{2+} + Co(N_4')(OH_2)Cl^{2+} \quad (11)$$
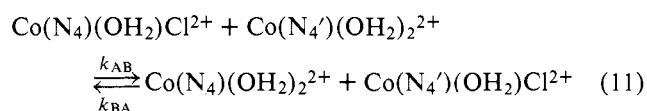
for N_4 = [14]tetraeneN$_4$ and N_4' = [14]dieneN$_4$, [14]py-dieneN$_4$, and [14]dieneN$_4$-one. For the case that N_4' = [14]dieneN$_4$ we have made use of the sensitivity of the methyl group chemical shifts to the ligation of cobalt(III) in order to investigate the stoichiometry of the reaction. Thus when a slight excess of $Co([14]dieneN_4)(OH_2)_2^{2+}$ was mixed with $Co([14]tetraeneN_4)(OH_2)Cl^{2+}$ ($\sim 8 \times 10^{-3}$ M) in 0.1 M $DClO_4$ (D_2O) we obtained the $Co([14]dieneN_4)(OH_2)Cl^{2+}$

Table III. Oxidations of $Co(N_4)(OH_2)_2^{2+}$ Complexes by Cobalt(III)-edta Species

oxidant	pH	k, M^{-1} s^{-1} ^{a}	
		[14]tetraeneN$_4$	[14]dieneN$_4$
Co(edtaH)Cl$^-$	0	$(2.3 \pm 0.2) \times 10^4$ (2)^b	550 ± 50 (2)^c
	0.3	1.4×10^4	
		$(9.4 \pm 0.8) \times 10^3$ (2)^b	
		$(8.9 \pm 0.9) \times 10^3$ (2)^c	
Co(edta)$^-$	0	8×10^{-2} ^{d}	$<3 \times 10^{-2}$ ^{d}
	1	3×10^{-2} ^{d}	
	2	2×10^{-3} ^{d}	

^{a} $\mu = 1$ ($HClO_4$, $NaClO_4$). ^{b} Co(edtaH)Cl$^-$ dissolved in acidic solution before mixing with $Co(N_4)(OH_2)_2^{2+}$. ^{c} Co(edtaH)Cl$^-$ dissolved in water before mixing with $Co(N_4)(OH_2)_2^{2+}$. ^{d} Based on initial rates.

spectrum.[43] Mixing $Co([14]dieneN_4)(OH_2)Cl^{2+}$ with a slight excess of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ resulted in the $Co([14]tetraeneN_4)(OH_2)Cl^{2+}$ spectrum.[43] Owing to the relatively large $Co([14]tetraeneN_4)(OH_2)Cl^{2+}/Co([14]tetraeneN_4)(OH_2)_2^{2+}$ self-exchange rate, a small excess of this cobalt(II) complex resulted in very appreciable broadening of the spectrum of the aquo-chloro complex. This effect has been utilized to obtain a direct measure of the $Co([14]tetraeneN_4)(OH_2)Cl^{2+}/Co([14]tetraeneN_4)(OH_2)_2^{2+}$ self-exchange rate. A plot of the NMR peak width at half-height vs. [Co(II)] (cobalt(II) concentration range (0.77-1.85) $\times$ 10^{-4} M) gave a value of k_{exch} = $(1.0 \pm 0.2) \times 10^5$ M^{-1} s^{-1} at 25 °C in 0.1 M HO_3SCF_3. Kinetic parameters for these reactions are summarized in Table V.

To ensure that reactions 11 were those observed for the relatively difficult to characterize [14]py-dieneN$_4$ and [14]-dieneN$_4$-one systems, we have also examined the much faster $Co(N_4')Cl_2^+ + Co([14]tetraeneN_4)(OH_2)_2^{2+}$ reactions; in 0.1 M HCl, 24 °C, the rate constants are $(1.4 \pm 0.1) \times 10^6$ and $(9.5 \pm 0.5) \times 10^4$ M^{-1} s^{-1}, respectively. We observed only one electron transfer rate for reactions of our $Co(N_4)(OH_2)Cl^{2+}$ complexes and would estimate that our preparations were at least 90% in the chloro-aquo form.

Discussion

As noted in detail below, oxidations of the $Co(N_4)(OH_2)_2^{2+}$ substrates by halo complexes always proceed at vastly greater (by factors of 10^4-10^6) rates than oxidants conventionally regarded as being outer sphere in transition-state geometry and having approximately the same driving force. When the driving force of these reactions is sufficiently large they reach a limiting rate about two orders of magnitude smaller than the diffusional limit. Furthermore, the $Co(N_4)(OH_2)_2^{2+}$ substrates catalyze the *first* hydrolysis step of $Co(N_4)X_2^+$ where the cobalt(III) products are known to anate very slowly. The only simple way of accounting for these observations is that the halo complexes oxidize the $Co(N_4)(OH_2)_2^{2+}$ substrates by means of inner-sphere electron-transfer pathways, while the other reagents considered react by outer-sphere pathways. The inner-sphere pathway has been experimentally verified for the {$Co([14]dieneN_4)(OH_2)Cl^{2+}+Co([14]tetraeneN_4)$-$(OH_2)_2^{2+}$} and {$Co([14]tetraeneN_4)(OH_2)Cl^{2+} + Co([14]-dieneN_4)(OH_2)_2^{2+}$} reactions.

The appropriate inner-sphere reaction pathways may be represented in terms of Scheme I. In the limit of no barrier to electron transfer within the inner-sphere precursor complex, the rate of electron transfer is limited only by the rate of $Co^{II}-OH_2$ bond breaking and $k_{obsd} = K_{OS}k_C$. The rate of reaction of $Co(N_4)(OH_2)_2^{2+}$ (N_4 = [14]tetraeneN$_4$ or [14]-dieneN$_4$) with CH_3 to form $Co(N_4)(OH_2)CH_3^{2+}$ is of the order of 10^8 M^{-1} s^{-1}.[44,45] This would be consistent with k_C $\sim 10^9$ s^{-1} for the rate of $Co^{II}-OH_2$ bond breaking, assuming

Table IV. $Co(N_4)(OH_2)_2^{2+}$-Catalyzed Hydrolyses of $Co(N_4)X_2^+$ [a]

| N_4	X	range of $10^5[Co(N_4)(OH_2)_2^{2+}]$, M	k_h, s^{-1} [b]	k_{h0}, s^{-1}	k_{Co}, M^{-1} s^{-1}
[14]tetraeneN$_4$	Cl	0.35–34.3	0.021, [c] 0.013 [d]	1 ± 1	$(8.0 ± 0.5) × 10^5$
[14]tetraeneN$_4$	Br	0.25–2.5	0.12 ± 0.02 [c]	0.9 ± 0.4	$(3.9 ± 0.5) × 10^5$
[14]dieneN$_4$	Cl	0.055–0.091	0.036 ± 0.003 [e]	0.05 ± 0.01	99 ± 6
[14]dieneN$_4$	Br	0.14–0.44	0.05 ± 0.02 [e]	0.07 ± 0.02	$(8 ± 1) × 10^4$

[a] All rate constants at 25 °C, μ = 0.1. See text and Table S1.[23] [b] Value of the independently determined acid hydrolysis rate constant of the cobalt(III) complex. Data from references cited. [c] Reference 12. [d] C. L. Wong, Ph.D. Dissertation, University of Hong Kong, 1976. [e] Reference 18d.

Table V. Kinetic Parameters for $Co([14]tetraeneN_4)(OH_2)Cl^{2+}$ + $Co(N_4')(OH_2)_2^{2+}$

| N_4'	$10^{-4} k_{AB}$, M^{-1} s^{-1}	$10^{-3} k_{BA}$, M^{-1} s^{-1}	$K_{AB} = k_{AB}/k_{BA}$	$10^{-3} k°_{AB} = (k_{AB}k_{BA})^{1/2}$, M^{-1} s^{-1}
[14]dieneN$_4$	0.15 ± 0.01 [b]	4.2 ± 0.2 [c]	0.36 ± 0.04	2.5 ± 0.3
[14]py-dieneN$_4$	16 ± 1	62 ± 2	2.6 ± 0.3	100 ± 6
[14]dieneN$_4$-one	16 ± 1	5.8 ± 0.4	28 ± 4	30 ± 3
[14]tetraeneN$_4$	10 ± 2 [d]	10 ± 2 [d]	1.00	10 ± 2

[a] 23.0 °C; μ = 0.1 (HClO$_4$); except as indicated. Rate constants are averages (and mean deviations) of two or more determinations with oxidant in excess and with [oxidant] varied by a factor of about 2. [b] $\Delta H^{\ddagger}$ = 26.4 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −96 J mol^{-1} deg^{-1}. [c] $\Delta H^{\ddagger}$ = 25.5 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −88 J mol^{-1} deg^{-1}. [d] Determined by the NMR line broadening technique in 0.1 M HO$_3$SCF$_3$ at 25 °C.

Scheme I
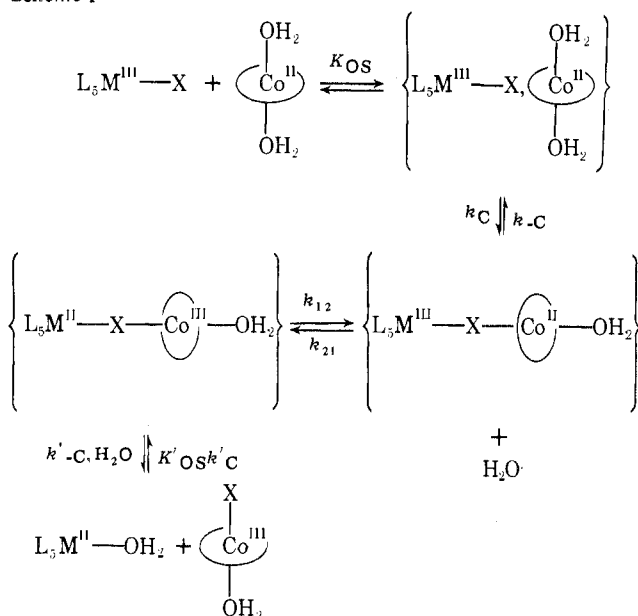
$K_{OS} \sim 0.15$ M^{-1}.[46] The reactions investigated in the present study are mostly slower than required for this limit (with $k_C \sim 10^9$ s^{-1}), even when differences in charge type are taken into account. We shall now consider the observed reaction patterns and the molecular properties which contribute to them.

The $Co(N_4)(OH_2)_2^{2+}$ catalysis of $Co(N_4)X_2^+$ hydrolyses is the consequence of the simple electron transfer reactions

$$Co(N_4)X_2^+ + H_2O + Co(N_4)(OH_2)^{2+}$$
$$\rightarrow Co(N_4)(OH_2)_2^{2+} + X^- + Co(N_4)(OH_2)X^{2+} \quad (12)$$
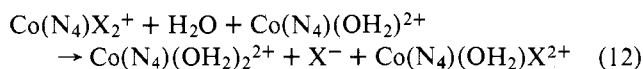
Since the cobalt(II) complexes are axially labile and have very little affinity for X$^-$ in aqueous solutions,[10] this reaction fits nicely into the pattern of Scheme I with the bridging halide ligand being transferred from one cobalt complex to the other. Substitution of Cl$^-$ for H$_2$O on these cobalt complexes should result in a relatively small (<0.1 V) change in the Co(III)–Co(II) reduction potential.[20] Yet the $Co([14]dieneN_4)$-$(OH_2)_2^{2+}$ reduction of $Co([14]dieneN_4)Cl_2^+$ is 10^6 faster than the $Co([14]dieneN_4)(OH_2)_2^{2+}$ reduction of $Co([14]$-dieneN$_4$)(OH$_2$)$_2^{3+}$; a 10^7 difference in reactivity is exhibited by the analogous [14]tetraeneN$_4$ complexes. Further to this

point, the $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ reaction with $Co([14]dieneN_4)(OH_2)Cl^{2+}$ (25 °C, μ = 0.1) proceeds at a rate 3 × 10^6 times faster than its reaction with $Co([14]$-dieneN$_4$)(OH$_2$)$_2^{3+}$ (25 °C, μ = 1.0; $\Delta G°$ ~ 0 for both reactions), and the $Co([14]tetraeneN_4)(OH_2)Cl^{2+}/Co([14]$-tetraeneN$_4$)(OH$_2$)$_2^{2+}$ self-exchange reaction is more than 3 × 10^6 faster (when differences of ionic strength are taken into account) than the $Co([14]tetraeneN_4)(OH_2)_2^{3+,2+}$ self-exchange. Thus the inner-sphere pathway affords an *intrinsic* reactivity advantage of a factor of 10^4–10^7 in these systems.

The reactivity advantage of the inner-sphere pathway, noted above for cobalt oxidants with macrocyclic ligands, is typical of reactions of low-spin $Co(N_4)(OH_2)_2^{2+}$ species as is shown by the rate constant ratios in Table VI, and by the linear free energy correlation of oxidations of the macrocyclic cobalt(II) complexes with oxidations of ruthenium(II) complexes in Figure 1. The rate constants in this figure have been corrected to an ionic strength of 0.1,[47–50] and linear corrections (i.e., we have neglected the quadratic term) of the rate constants of oxidations of $Co([14]dieneN_4)(OH_2)_2^{2+}$ and $Ru(NH_3)_5$-py^{2+} have been made using literature parameters and eq 1 (for $Co([14]dieneN_4)(OH_2)_2^{2+}$, E^0 = 0.60 V, k_{exch} = 3 × 10^{-5} M^{-1} s^{-1};[16] for $Co([14]tetraeneN_4)(OH_2)_2^{2+}$, E^0 = 0.60 V, k_{exch} = 0.06 M^{-1} s^{-1};[16] for $Ru(NH_3)_5py^{2+}$, E^0 = 0.30 V, k_{exch} = 4.7 × 10^5 M^{-1} s^{-1};[51,52] for $Ru(NH_3)_6^{2+}$, E^0 = 0.05 V,[53,54] k_{exch} = 4.3 × 10^3 M^{-1} s^{-1} [55]) so that all the oxidations are in effect referenced to $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ or $Ru(NH_3)_6^{2+}$. The reactions which are constrained to be outer sphere with $Co(N_4)(OH_2)_2^{2+}$ are all relatively slow and, with the exception of the data for $Ru(bpy)_3^{3+}$ reactions, cluster around a correlation line of unit slope, as one would predict based on (1). The $Ru(bpy)_3^{3+}$ oxidations of $Ru(NH_3)_6^{2+}$ appear to be diffusion rather than activation limited;[55] also the quadratic contributions to (1) probably do not cancel (for Co(II) vs. Ru(II)) when the driving force is very large. Hence this large deviation is to be expected. The halide-mediated reactions are more scattered, possibly owing to variations in the contributions of the first two steps in Scheme I, but they also cluster around a correlation line of unit slope. Therefore the intrinsic advantage of the inner-sphere pathway for oxidation of low-spin $Co(N_4)(OH_2)_2^{2+}$ can be regarded as a general feature of the reactions of σ^*-acceptor oxidants, and the corresponding rate advantage is at least a factor of 10^6.
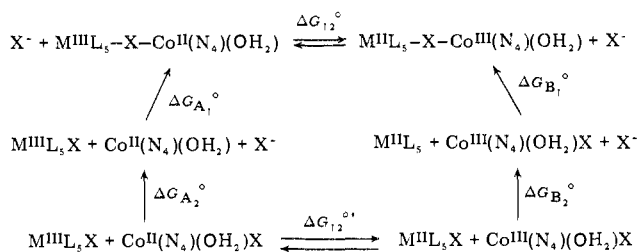
The approximate free-energy correlation (Figure 1) of inner-sphere oxidations of $Co(N_4)(OH_2)_2^{2+}$ with outer-sphere oxidations of $Ru(NH_3)_5A^{2+}$ (A = NH$_3$ or py) suggests that

Table VI. Ratio of Rate Constants for Inner- and Outer-Sphere Reactions

|	$CoCl^{2+}/$ Co^{3+}	$MnCl^{2+}/$ Mn^{3+}	$Co(edtaH)$- $Cl^-/$ $Co(edta)^-$	$Co(N_4)$- Cl_2^+ [a]$/$ $Co(N_4)$- $(OH_2)_2^{3+}$
$Co([14]tetraeneN_4)$- $(OH_2)_2^{2+}$	$\geq 4 \times$ 10^4 [b]	$\geq 1 \times$ 10^2 [b]	$\sim 3 \times 10^5$	$\sim 2 \times 10^5$
$Co([14]dieneN_4)$- $(OH_2)_2^{2+}$	$\geq 2 \times$ 10^4 [b]	$\geq 5 \times$ 10^2 [b]	$> 2 \times 10^4$	$\sim 5 \times 10^4$

[a] Corrected for ionic strength and charge type differences (see ref 47). [b] Oxidations with MCl^{2+} probably occur at a rate limited by the rate of $Co-OH_2$ bond breaking (see text). The actual value of k_{12} would very likely be larger than that inferred from k_{obsd}.

Scheme II

$$X^- + M^{III}L_5-X-Co^{II}(N_4)(OH_2) \underset{}{\overset{\Delta G_{12}^\circ}{\rightleftharpoons}} M^{II}L_5-X-Co^{III}(N_4)(OH_2) + X^-$$

$$\diagup \Delta G_{A_1}^\circ \qquad\qquad \diagdown \Delta G_{B_1}^\circ$$

$$M^{III}L_5X + Co^{II}(N_4)(OH_2) + X^- \qquad M^{II}L_5 + Co^{III}(N_4)(OH_2)X + X^-$$

$$\Big\uparrow \Delta G_{A_2}^\circ \qquad\qquad \Big\uparrow \Delta G_{B_2}^\circ$$

$$M^{III}L_5X + Co^{II}(N_4)(OH_2)X \underset{}{\overset{\Delta G_{12}^{\circ\prime}}{\rightleftharpoons}} M^{II}L_5X + Co^{III}(N_4)(OH_2)X$$

similar factors contribute to the relative reactivity in both classes of reactions. That the correlation is improved by referencing the reactions of $Co([14]dieneN_4)(OH_2)_2^{2+}$ to those of $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ using corrections based on (1) speaks to the same point. The limit of weak interaction between reaction centers gives rise to an intrinsic barrier (λ_{12}) which is modified by the free energy of reaction as in eq 1. The intrinsic difference in reactivity between $Co([14]dieneN_4)$-$(OH_2)_2^{2+}$ and $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ (note that the $Co(III)-Co(II)$ couples have the same potential)[16] appears to be comparably manifested in the rates of outer-sphere and inner-sphere reactions.

A systematic investigation of the free-energy dependence of inner-sphere reactions is somewhat more complex than for outer-sphere reactions. The most appropriate free-energy relation should be defined in terms of the reaction

$$M^{III}L_5-X-Co^{II}(N_4)(OH_2)^{4+}$$
$$\rightleftharpoons M^{II}L_5-X-Co^{III}(N_4)(OH_2)^{4+}, \Delta G_{12}^\circ \quad (13)$$
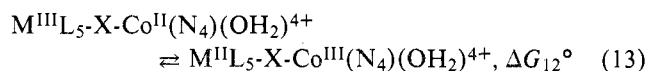
Direct measurement of ΔG_{12}° for this reaction is obviously not possible for systems as labile as ours. It is possible, however, to set up a thermodynamic cycle in terms of reactions which may be measured directly or about which some reasonable estimates may be made of the parameters of interest as in Scheme II. The relevant free-energy changes are then given by reactions 14-18, and eq 19 gives the expression for ΔG_{12}°. The first term, $\Delta G_{12}^{\circ\prime}$, can be measured directly or can be calculated from data available for the corresponding aquo ions and the stability constants for the halo complexes. The middle term can be viewed as the difference in the free energy of binding some complex ligand (the other reactant) to the five-coordinate M(II) complexes. The last term is the difference in free energy for the loss of X^- from M(II) and Co(II) complexes. As a first approximation the second and third terms will be neglected.[56] In most of the metal(II) complexes used in this study the bond to the X ligand is very weak and therefore the second and third terms should be very small. For very similar complexes the errors introduced by this approximation should be nearly constant, so the relative free-energy changes should
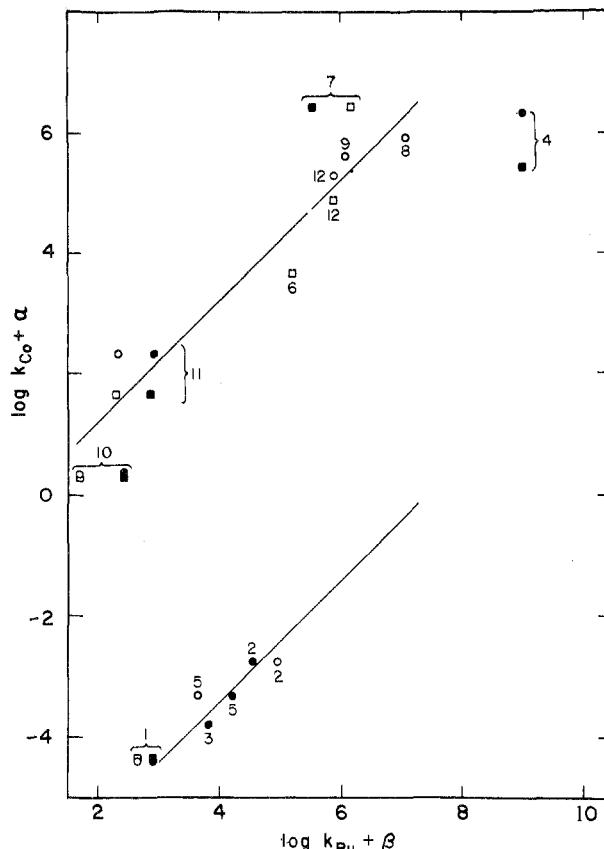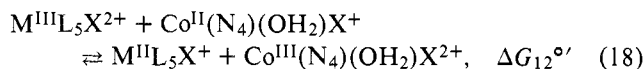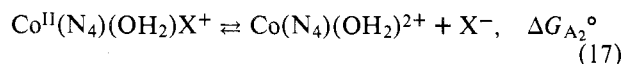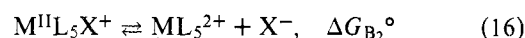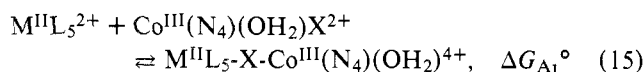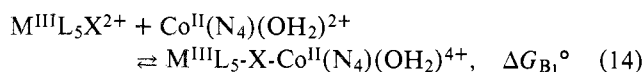

Figure 1. Correlation of rates of oxidations of cobalt(II) and ruthenium(II) complexes. All rate constants are adjusted to an ionic strength of 0.1 using the procedure described in ref 47-50. The values of α and β have been chosen based on eq 1, neglecting the quadratic term, and data from ref 16, 51, and 52: for $Ru(NH_3)_6^{2+}$, $\beta = 0$; for $Ru(NH_3)_5py^{2+}$, $\beta = 1.09$; for $Co([14]tetraeneN_4)(OH_2)_2^{2+}$, $\alpha = 0$; for $Co([14]dieneN_4)(OH_2)_2^{2+}$, $\alpha = 1.65$. Lines of slope 1.0 have been drawn through the data points: upper line for inner-sphere reactions; lower line for outer-sphere reactions. Oxidations of $Ru(NH_3)_6^{2+}$, closed figures; $Ru(NH_3)_5py^{2+}$, open figures; $Co([14]tetraeneN_4)(OH_2)_2^{2+}$, circles; $Co([14]dieneN_4)(OH_2)_2^{2+}$, squares. Oxidants: 1, $Co([14]dieneN_4)(OH_2)_2^{3+}$ (ref 18g, this study, and ref 16); 2, $Co([14]tetraeneN_4)(OH_2)_2^{3+}$ (ref 18a and this study); 3, $Co(edta)^-$ (ref 18a and this study); 4, $Ru(bpy)_3^{3+}$ (ref 55 and 18b); 5, $Co(phen)_3^{3+}$ (ref 51 and 18b); 6, $Co([14]dieneN_4)Cl_2^+$ (this study); 7, $Co([14]dieneN_4)Br_2^+$ (this study); 8, $Co([14]tetraeneN_4)Cl_2^+$ (this study); 9, $Co([14]tetraeneN_4)Br_2^+$ (this study); 10, $Co(NH_3)_5Cl^{2+}$ (this study); 11, $Co(NH_3)_5Br^{2+}$ (this study); 12, $Co(edtaH)Cl^-$ (this study).

not be affected significantly.

$$M^{III}L_5X^{2+} + Co^{II}(N_4)(OH_2)^{2+}$$
$$\rightleftharpoons M^{III}L_5-X-Co^{II}(N_4)(OH_2)^{4+}, \quad \Delta G_{B_1}^\circ \quad (14)$$

$$M^{II}L_5^{2+} + Co^{III}(N_4)(OH_2)X^{2+}$$
$$\rightleftharpoons M^{II}L_5-X-Co^{III}(N_4)(OH_2)^{4+}, \quad \Delta G_{A_1}^\circ \quad (15)$$

$$M^{II}L_5X^+ \rightleftharpoons ML_5^{2+} + X^-, \quad \Delta G_{B_2}^\circ \quad (16)$$

$$Co^{II}(N_4)(OH_2)X^+ \rightleftharpoons Co(N_4)(OH_2)^{2+} + X^-, \quad \Delta G_{A_2}^\circ \quad (17)$$

$$M^{III}L_5X^{2+} + Co^{II}(N_4)(OH_2)X^+$$
$$\rightleftharpoons M^{II}L_5X^+ + Co^{III}(N_4)(OH_2)X^{2+}, \quad \Delta G_{12}^{\circ\prime} \quad (18)$$

$$\Delta G_{12}^\circ = \Delta G_{12}^{\circ\prime} + (\Delta G_{B_1}^\circ - \Delta G_{A_1}^\circ)$$
$$+ (\Delta G_{B_2}^\circ - \Delta G_{A_2}^\circ) \quad (19)$$

The data for inner-sphere $Co(N_4)(OH_2)_2^{2+}$ reduction of σ^* donors is summarized in Figure 2. Despite the uncertainty in our knowledge of the oxidizing potentials (E_{ox}° or $\Delta G_{ox}^{\circ\prime}$) (for most of the $M^{III}L_5X/M^{II}L_5X$ couples this is probably of
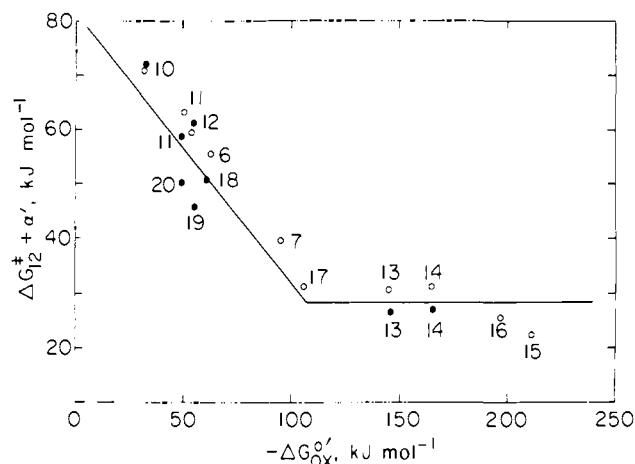
Figure 2. Approximate free energy correlation for inner-sphere Co(N₄)-(OH₂)₂²⁺ reductions of complexes with σ*-acceptor orbitals. Ionic strength corrections applied as in Figure 1. A linear correction of 9.5 kJ mol⁻¹ has been added to $\Delta G^{\ddagger}_{12}$ for most Co([14]tetraeneN₄)(OH₂)₂²⁺ reactions to compensate for λ_{11} differences between this and the Co([14]dieneN₄)-(OH₂)₂²⁺ system; no such correction has been made for the CoCl²⁺ and MnCl²⁺ reactions, since the rates of these reactions appear to depend on the rate of substitution on Co(N₄)(OH₂)₂²⁺. For Co(N₄)X₂⁺, Co(NH₃)₅X²⁺, MX²⁺, and Co(edtaH)X⁻ the values of ΔG°_{ox} have been estimated from data in ref 20 (e.g., replacing H₂O by Cl⁻ appeared to increase E° by about 0.03 V). Oxidants: 6, Co([14]dieneN₄)Cl₂⁺; 7, Co([14]dieneN₄)Br₂²⁺; 10, Co(NH₃)₅Cl²⁺; 11, Co(NH₃)₅Br²⁺; 12, Co(edtaH)Cl⁻; 13, MnCl²⁺; 14, CoCl²⁺; 15, Cl₂⁻ (data from ref 30); 16, Br₂⁻ (data from ref 30); 17, I₂⁻ (data from ref 30); 18, Co([14]-dieneN₄)(OH₂)Cl²⁺; 19, Co([14]py-dieneN₄)(OH₂)₂Cl²⁺. Reductants: ○, Co([14]dieneN₄)(OH₂)₂²⁺; ●, Co([14]tetraeneN₄)(OH₂)₂²⁺. The upper line is drawn with a slope of 0.5.

the order of ±(5–10) kJ mol⁻¹), Figure 2 demonstrates a strong correlation of $\Delta G^{\ddagger}_{12}$ with $\Delta G^{\circ\prime}_{ox}$ (or with $\Delta G^{\circ\prime}_{12}$). Furthermore, there are two distinct classes of inner-sphere oxidants: (1) with $-\Delta G^{\circ}_{ox} < 100$ kJ mol⁻¹ for which $\Delta G^{\ddagger}_{12}$ is proportional to $-\Delta G^{\circ\prime}_{ox}$; and (2) with $-\Delta G^{\circ\prime}_{ox} > 100$ kJ mol⁻¹ for which $\Delta G^{\ddagger}_{12}$ is independent of $\Delta G^{\circ\prime}_{ox}$. Neglect of the variations in intrinsic (λ) factors no doubt leads to scatter in the free energy dependent region, but the points cluster around a line of slope ~0.5 as in (1). In the limiting region ($-\Delta G^{\circ\prime}_{ox} > 100$ kJ mol⁻¹) the observed rate constants run one to two orders of magnitude smaller than the expected diffusional limit and are consistent with the rate of reaction being limited by the rate of substitution into the inner coordination shell of Co(N₄)(OH₂)₂²⁺. Related substitution-limited behavior, and the effect on free-energy correlations, has been found and discussed for V²⁺.[2,7,57,58] In this limit $k_{obsd} = K_{OS}k_C$; our limit implies that $k_{obsd} \sim 10^6$ M⁻¹ s⁻¹, which is consistent with $k_C \sim 10^9$ s⁻¹.

Since $\Delta G^{\ddagger}_{12}$ has about the expected free-energy dependence for small ΔG°_{12} (i.e., for $-\Delta G^{\circ\prime}_{ox} < 100$ kJ mol⁻¹), one might also expect to see manifestations of the quadratic term in (1) for $\Delta G^{\circ}_{ox} \ll -100$ kJ mol⁻¹. That the reaction rates do not become slow again for very large driving forces may be a manifestation of the quantum mechanical effects expected under such conditions.[59]
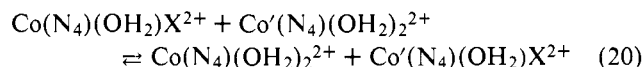
Our data for the IrCl₆²⁻ oxidation of Co([14]tetraeneN₄)-(OH₂)₂²⁺ deviate significantly from the pattern of the data in Figure 2. The observation of $\Delta G^{\ddagger}_{12}$ larger than expected is consistent with a large positive contribution to $\Delta G^{\circ}_{B_2}$ in eq 19, since IrCl₆³⁻ is a substitution-inert species. As a consequence ΔG°_{12} would be correspondingly less negative and $\Delta G^{\circ}_{B_2} > \Delta G^{\circ}_{A_2}$.[60]

There is an interesting inversion of reactivity patterns among the Co(N₄)X₂⁺/Ru(NH₃)₅py²⁺ and Co(N₄)X₂⁺/Co(N₄)-(OH₂)₂²⁺ reactions. Thus the "normal" order of the chloro
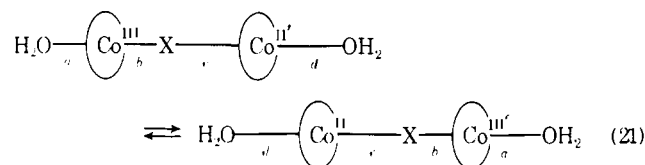
complex being less reactive than the bromo complex is observed for N₄ = [14]dieneN₄, while the "inverted" order of bromo more reactive than the chloro complex is observed for [14]-tetraeneN₄. In fact the formation constants (X⁻ + Co(N₄)-(OH₂)X²⁺ ⇌ Co(N₄)X₂⁺ + H₂O) follow the same trend,[12] and the patterns of the electron transfer reactions most likely follow the resulting variations in ΔG°_{12}.

The evidence cited above clearly demonstrates that, despite the much smaller activation barrier for the inner-sphere pathway, there is a typical "Franck-Condon" barrier to electron transfer in halide-bridged, σ*-donor–σ*-acceptor systems. Thus the relative reactivities of outer-sphere and inner-sphere pathways respond in very similar ways to changes in ΔG°_{12} and to changes in "intrinsic" factors, insofar as the latter are probed by the cobalt-[14]dieneN₄ and [14]tetraeneN₄ systems. For either pathway, such scatter as exists in the linear free energy correlations can be attributed to the inaccuracies of eq 1 in predicting the "intercepts" of free-energy correlations,[2,18a c,51,61] to uncertainty in our knowledge of ΔG°_{12}, or to neglect of differences in intrinsic reorganizational parameters (λ).

Some additional considerations help elucidate the source of the huge rate advantage of the inner-sphere pathway. It is helpful in these considerations to formulate an "inner-sphere self-exchange" reaction appropriate to our systems. This is readily accomplished by replacing M^{III}L₅X in Scheme I by Co(N₄)(OH₂)X²⁺, so that the equation

$$Co(N_4)(OH_2)X^{2+} + Co'(N_4)(OH_2)_2^{2+}$$
$$\rightleftharpoons Co(N_4)(OH_2)_2^{2+} + Co'(N_4)(OH_2)X^{2+} \quad (20)$$

describes the overall reaction (the prime is employed merely to label one of the exchange partners) and the electron transfer step may be described as in eq 21. Our X-ray structural stud-

ies[10,14] demonstrate that the low-spin cobalt(II) species are greatly distorted along the unique axis. Furthermore, the available structural and kinetic evidence suggests that the very weak axial bonding in the cobalt(II) systems may be approximately described in terms of a three-center five-electron bonding model.[10] The Co(N₄)(OH₂)X²⁺ ligand is a very weak base, and as a consequence the three-center bonding model would imply that the Co^{II}-OH₂ bond length (d) is shorter in the inner-sphere precursor complex than in Co(N₄)(OH₂)₂³⁺, and that $c > d$.[10] Furthermore, b must be less than c and a less than d. Since the force constants for the Co–Cl and Co–Br vibrations are smaller than the force constants of the Co–OH₂ vibrations,[62] and as a result of the postulated contraction of the Co^{II}-OH₂ bond length in the precursor complex, the inner sphere reorganizational barrier, $\lambda_i(IS)$, for the electron transfer step (21) will necessarily be smaller than $\lambda_i(OS)$ for the outer-sphere precursor complex in the Co(N₄)(OH₂)₂³⁺/Co(N₄)(OH₂)₂²⁺ self-exchange.

Our observations are in support of these arguments. Thus the difference in $\Delta H^{\ddagger}_{12}(OS)$ for reduction of Co([14]-dieneN₄)(OH₂)₂³⁺ and Co([14]tetraeneN₄)(OH₂)₂³⁺, or in $\Delta H^{\ddagger}_{12}$ (IS) for oxidation of Co([14]dieneN₄)(OH₂)₂²⁺ and Co([14]tetraeneN₄)(OH₂)₂²⁺ should directly reflect the difference in λ_i for the macrocyclic complexes.[63,64] For the outer-sphere reductions with Ru(NH₃)₅py²⁺, $\Delta[\Delta H^{\ddagger}_{12} (OS)] = 25 \pm 10$ kJ mol⁻¹; and for the inner-sphere oxidations with Co(NH₃)₅Br²⁺, $\Delta[\Delta H^{\ddagger}_{12} (IS)] = 5 \pm 6$ kJ mol⁻¹.[65] It is interesting that the appreciable difference in reactivity of the

Table VII. Components of the Activation Barrier for Inner-Sphere and Outer-Sphere Self-Exchange Reactions of Cobalt-[14]-tetraeneN$_4$ Complexes

	energies, kJ mol^{-1}	
	outer sphere[a]	inner sphere[b]
$\Delta G^{\ddagger}_{AA}$ (obsd)[c]	69.8	34.3
ΔG_i	37.6[d]	19[e]
ΔG_o	16.8[f]	<10[g]
Δw	1.4[f]	>5[f,i]
	11[g]	<16[i]
$-RT \ln \kappa$[j]	4–14	0

[a] For the Co([14]tetraeneN$_4$)(OH$_2$)$_2$$^{3+,2+}$ self-exchange; 25 °C, μ = 1.0; ref 16. [b] For the Co([14]tetraeneN$_4$)(OH$_2$)Cl^{2+} + Co([14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$ self-exchange; 25 °C; μ = 0.1; this work. [c] Using $k_{12} = Ze^{-\Delta G^{\ddagger}_{12}/RT}$, $Z = 10^{11}$ M^{-1} s^{-1}. This has the effect of setting $\Delta w' = RT \ln K'_{OS}$ for outer-sphere reactions and $\Delta w = -RT \ln K_{OS}k_C$ for inner-sphere reactions. All energies in kJ mol^{-1} [d] Using 1.913 (2.5 × 10^5 dyn cm^{-1}) and 2.29 Å (0.56 × 10^5 dyn cm^{-1}) for the Co^{III}-OH$_2$ and Co^{II}-OH$_2$ bond lengths (and force constants), respectively. Bond lengths are based on X-ray crystallographic determinations.[10,14] The force constants are based on a tentative assignment of Raman frequencies at 485 (Co^{III}) and 226 cm^{-1} (Co^{II}) (J. F. Endicott and W. H. Woodruff, work in progress) and comparisons with ammine complexes; see K. H. Schmidt and A. Müller, *Coord. Chem. Rev.*, **19**, 41 (1976). [e] From ΔG_i(IS) = $\frac{1}{2}\Delta G_i$(OS) + constant (see Figure 3). [f] Using^3 ΔG_o(OS) = $e^2/4[(1/2a) + (1/2b) - (1/r)][(1/D_{op}) - (1/D_s)]$ and a mean radius of $a = b = 6$ Å and $r = 9.4$ Å based on crystallographic data.[10,14,16] These parameters give a mean distance of closest approach $\bar{r} = 11.1$ Å. Numerical values of ΔG_o and Δw based on parameters in G. M. Brown and N. Sutin, *J. Am. Chem. Soc.*, submitted. [g] By inference: $\Delta G_o = \Delta G^{\ddagger}_{12} - \Delta G_i - \Delta w$. [h] For $K'_{OS} \sim 10^{-2}$ M^{-1} (25 °C, μ = 1.0). [i] Assuming that k_C depends on the rate of water loss, $\sim 10^9$ s^{-1} from Co(N$_4$)(OH$_2$)$_2$$^{2+}$, 10^{13} s$^{-1} \geq k_{-C} > 10^9$ s^{-1}, $K_{OS} \sim 0.01$ M^{-1} (25 °C, μ = 0.1). The upper limit is based on $\Delta G^{\ddagger}_{AA} = 34.3$ kJ mol$^{-1} = \Delta G_i + \Delta G_o + \Delta w - RT \ln \kappa$, assuming that $\Delta G_i = 19$ kJ mol^{-1} and $\Delta G_o = 0$. [j] Inferred transmission coefficient (κ). Based on $\Delta G^{\ddagger}_{AA} = 69.8$ kJ mol$^{-1} = \Delta G_i + \Delta G_o + \Delta w - RT \ln \kappa$.

[14]dieneN$_4$ and [14]tetraeneN$_4$ complexes is not clearly manifested as an enthalpy of activation in the inner-sphere reactions.[66] This could be consistent with some relaxation of strain at the essentially "five"-coordinate cobalt(II) center in the inner sphere precursor complex for the [14]dieneN$_4$ ligand, with nonequivalent entropy contributions to $\Delta G^{\circ}_{A_2}$ and $\Delta G^{\circ}_{A_1}$ arising due to the relative bulk of the incoming M^{III}L$_5$X "ligand". Similar strain relaxation effects appear to contribute positive terms to the entropy of activation for hydrolysis reactions of these and related complexes.[11,12,18d,67-69]

On a more quantitative level, reactions 11 permit evaluation of the intrinsic parameters for the inner-sphere reactions. Using the free energy independent rate constants from Table V,[70] we may calculate the ΔG°_{AB} independent activation free energy, $\Delta G^{\ddagger}_{AB}$ (IS; $\Delta G^{\circ} = 0$) = λ_{AB} (IS)/4, for these reactions. We have elsewhere determined that the differences in $\Delta G^{\ddagger}_{AB}$ (OS) for the outer-sphere Co(N$_4'$)(OH$_2$)$_2$$^{3+/2+}$ self-exchange reactions are correlated to variations in Co^{II}-OH$_2$ bond lengths and therefore are due to the differences in λ_i (OS).[14,16] Figure 3 demonstrates a clear relationship between $\Delta G^{\ddagger}_{AB}$ (IS; ΔG° = 0) for the {Co([14]tetraeneN$_4$)(OH$_2$)Cl^{2+} + Co(N$_4'$)-(OH$_2$)$_2$$^{2+}$} reactions and $\Delta G^{\ddagger}_{BB}$ (OS). The "intercept"[71] in Figure 3 is $\frac{1}{2}\Delta G^{\ddagger}_{AA}$ (IS), based on the usual assumption $\Delta G^{\ddagger}_{AB}$ (IS; ΔG° = 0) = $\frac{1}{2}$ [$\Delta G^{\ddagger}_{AA}$ (IS) + $\Delta G^{\ddagger}_{BB}$ (IS)].[2-4] The intercept is thus an experimental number based on k_{AA}. In view of the importance of this number, it is to be noted that our experimental value of $k_{AA} = (1.0 \pm 0.2) \times 10^5$ M^{-1} s^{-1} is in excellent agreement with the value of $k_{AA} = 8 \times 10^4$ M^{-1} s^{-1} based on data from Table V and the Co(NH$_3$)$_5$Cl^{2+} oxidations of Co([14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$ and Co([14]-dieneN$_4$)(OH$_2$)$_2$$^{2+}$.[70] Since $\Delta G^{\ddagger}$ (IS; ΔG° = 0) =
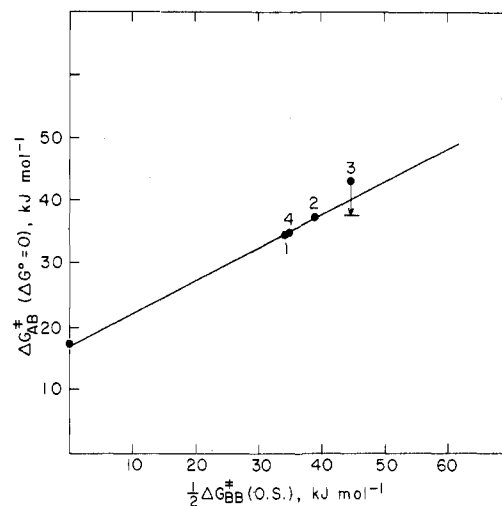

Figure 3. Correlation of intrinsic reorganizational parameters ($\lambda = 4\Delta G^{\ddagger}$) of inner-sphere, $\Delta G^{\ddagger}_{AB}(\Delta G^{\circ} = 0)$, and outer-sphere, $\Delta G^{\ddagger}_{BB}$(OS), electron-transfer reactions of macrocyclic complexes. Values of $\Delta G^{\ddagger}_{BB}$(OS) are for Co(N$_4'$)(OH$_2$)$_2$$^{3+,2+}$ self-exchange reactions (ref 16; μ = 1.0, 25 °C); values of $\Delta G^{\ddagger}_{AB}(\Delta G^{\circ} = 0)$ are based on k°_{AB} from Table V (23 °C, μ = 0.1). For N$_4'$ = [14]py-dieneN$_4$, 1; [14]dieneN$_4$-one, 2; [14]dieneN$_4$, 3; [14]tetraeneN$_4$, 4. The vertical arrow for the Co([14]dieneN$_4$)-(OH$_2$)$_2$$^{2+}$ reduction of Co([14]tetraeneN$_4$)(OH$_2$)Cl^{2+} indicates a correction for the entropic (or steric) component of $\Delta G^{\ddagger}_{AB}(\Delta G^{\circ} = 0)$ (see text). The intercept is determined by $\frac{1}{2}\Delta G^{2-}_{AA}$(IS) for the Co([14]-tetraeneN$_4$)(OH$_2$)Cl^{2+}/Co([14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$ self-exchange (see text).

$0.25\Delta G^{\ddagger}_{BB}$(OS) + $0.5\Delta G^{\ddagger}_{AA}$(IS), Figure 3 shows that λ_i(IS) $\simeq \frac{1}{2} \lambda_i$(OS).

In Table VII we have summarized and contrasted the components of the activation free energy in the Co([14]-tetraeneN$_4$)(OH$_2$)$_2$$^{3+,2+}$ and the Co([14]tetraeneN$_4$)-(OH$_2$)Cl^{2+}/Co([14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$ reactions. We have shown that differences in ΔG_i(OS) and ΔG_i (IS) account for only about half the difference observed between $\Delta G^{\ddagger}_{AA}$(OS) and $\Delta G^{\ddagger}_{AA}$(IS). We infer that an additional advantage of the inner-sphere pathway arises because ΔG°(IS) is probably near zero for these systems.[71] These two effects (i.e., reductions in the magnitudes of the reorganizational parameters, λ_i and λ_o) easily account for a factor of $\sim 10^5$ in the approximately 3 × 10^6 rate advantage of the inner-sphere self-exchange reaction. The remaining small factor can be attributed to the greater adiabaticity (i.e., transmission coefficient, $\kappa \sim 1$) of the inner-sphere pathway.[73]

Conclusions

Our study of halide-bridged inner-sphere electron-transfer reactions using a series of low-spin macrocyclic cobalt(II) complexes in which axial bond lengths vary has demonstrated the following points.

1. The inner-sphere pathway in these σ^*-σ^* electron-transfer reactions has about a 10^6-fold intrinsic rate advantage over the outer-sphere pathway.

2. This rate advantage has been shown to derive from the following factors (in order of decreasing importance): (a) a smaller inner-sphere reorganizational barrier (λ_i) for the inner-sphere pathway; for a Cl$^-$ bridge, λ_i(IS) $\simeq \frac{1}{2} \lambda_i$(OS); (b) the solvent reorganizational barrier (λ_o) approaches zero; (c) the inner-sphere reactions may be somewhat more adiabatic than the corresponding outer-sphere reactions.

3. The usual free-energy correlations hold at least approximately, with $\Delta G^{\ddagger} \propto 0.5\Delta G^{\circ}$ until the rates become substitution limited.

Our limited observations on bromide bridged systems suggest that λ_i(IS) will be only slightly smaller than $\frac{1}{2}\lambda_i$(OS)

for these systems. It will be of interest to explore these systems further to determine how much of the reduction in λ_i originates in the correlation of the motion of the bridging ligand from Co(III) to Co(II).[74] At present there is no reason to believe in the generality of the $\lambda_i(\text{IS}) = \frac{1}{2}\lambda_i(\text{OS})$ relationship for cobalt systems. This relationship does not seem consistent with data on Cr(III)/Cr(II) self-exchange reactions.[75] The reduction of $\lambda_i(\text{IS})$ relative to $\lambda_i(\text{OS})$ is very likely a function of both the bridging ligand (X) and the counter reagent (ML$_5$).

It is clear from our observations that mechanistic inferences based on simple linear free energy correlations can be grossly in error owing to the differences in dependencies of inner-sphere and outer-sphere reactions on the driving force ($\Delta G^{\ddagger} \propto 0.5\Delta G^{\circ}$, for both classes of reaction) and reorganizational parameters ($\lambda(\text{IS}) < \lambda(\text{OS})$). Thus plots of log $k(\text{A})$ vs. log $k(\text{B})$ for cobalt(III) complex oxidations of different reductants, A and B, could have slopes spanning much of the range between zero and one depending on whether the reactions were inner sphere or outer sphere and whether the differences in reactivity were dominated by ΔG° or reorganizational parameters.

Supplementary Material Available: Figures of ^{1}H NMR spectra, a table of absorption spectra, and a table of the kinetics of cobalt(II)-catalyzed hydrolyses of Co^{III}(N$_4$)X$_2$ (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Partial support of this research by the National Institutes of Health (Grant AM 14341) and by Wayne State University Graduate Fellowships (to B.D.) is gratefully acknowledged. (b) Preliminary reports of this research were presented at the 162nd (INOR-045) and 177th (INOR-168) National Meetings of the American Chemical Society, Washington, D.C., Sept 1971, and San Francisco, Calif., Sept 1976, respectively.

(2) For recent reviews see (a) R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One,* **9**, 303 (1971); (b) R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two,* **9**, 173 (1974); (c) R. G. Linck, *Surv. Prog. Chem.,* **7**, 89 (1976); (d) N. Sutin in "Inorganic Biochemistry", Vol. 2, G. L. Eichorn, Ed., American Elsevier, New York, N.Y., 1973, Chapter 19, p 611; (e) R. G. Wilkins, "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, Chapter 5, p 252; (f) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, N.Y., 1970; (g) A. Haim, *Acc. Chem. Res.,* **8**, 264 (1975).

(3) (a) R. A. Marcus, *Annu. Rev. Phys. Chem.,* **15**, 155 (1964); (b) *J. Phys. Chem.,* **67**, 853 (1963); (c) *Discuss. Faraday Soc.,* **29**, 21 (1960).

(4) (a) N. S. Hush, *Trans. Faraday Soc.,* **57**, 557 (1961); (b) *Prog. Inorg. Chem.,* **8**, 391 (1967); (c) *Electrochim. Acta,* **13**, 1005 (1968).

(5) C. Bifano and R. G. Linck, *J. Am. Chem. Soc.,* **89**, 3945 (1967).

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

(7) N. Sutin, *Acc. Chem. Res.,* **1**, 225 (1968).

(8) F. F. Fan and E. S. Gould, *Inorg. Chem.,* **13**, 2647 (1974).

(9) $k_{obsd} = Z \exp(-\Delta G^{\ddagger}_{12}/RT)$; $\lambda_{12} = (\lambda_o)_{12} + (\lambda_i)_{12}$; $Z \sim 10^{11}$ M^{-1} s^{-1}.

(10) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.,* **99**, 429 (1977).

(11) J. F. Endicott and B. Durham, in "Chemistry of Macrocyclic Compounds", G. A. Melson, Ed., Plenum Press, New York, N.Y., in press, Chapter 6.

(12) D. P. Rillema, J. F. Endicott, and J. Barber, *J. Am. Chem. Soc.,* **95**, 6987 (1973).

(13) (a) H. Taube, H. Myers, and R. L. Rich, *J. Am. Chem. Soc.,* **75**, 4118 (1953); (b) H. Taube and H. Myers, *ibid.,* **76**, 2103 (1954).

(14) (a) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Am. Chem. Soc.,* **95**, 5097 (1973); (b) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *ibid.,* **96**, 5661 (1974); (c) M. D. Glick, T. J. Anderson, B. Durham, and J. F. Endicott, unpublished work.

(15) Ligand abbreviations: [14]tetraeneN$_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; [14]dieneN$_4$ = 5,7,7,12,-14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; [14]-dieneN$_4$-one = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-dien-6-one; [14]py-dieneN$_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]hepta-1(17),2,11,13,15-pentane; bpy = 2,2'-bi-pyridine; py = pyridine; edta = ethylenediamine tetraacetate.

(16) B. Durham, Ph.D. dissertation, Wayne State University, 1977.

(17) S. C. Jackels, K. Farmery, E. K. Barefield, N. Rose, and D. H. Busch, *Inorg. Chem.,* **11**, 2893 (1972).

(18) (a) D. P. Rillema, J. F. Endicott, and R. C. Patel, *J. Am. Chem. Soc.,* **94**, 394 (1972); (b) D. P. Rillema and J. F. Endicott, *ibid.,* **94**, 8711 (1972); (c) *Inorg. Chem.,* **11**, 236 (1972); (d) J. A. Kernohan and J. F. Endicott, *ibid.,* **9**, 1504

(1970); (e) N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.,* **88**, 5468 (1966); (f) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.,* **6**, 770 (1967); (g) M. P. Liteplo and J. F. Endicott, *ibid.,* **10**, 1420 (1971).

(19) K. M. Long and D. H. Busch, *J. Coord. Chem.,* **4**, 113 (1974).

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

(21) B. Durham, T. J. Anderson, J. A. Switzer, J. F. Endicott, and M. D. Glick, *Inorg. Chem.,* **16**, 271 (1977).

(22) C. L. Wong, Ph.D. Dissertation, University of Hong Kong, 1976.

(23) See paragraph at end of paper regarding supplementary material.

(24) H. Diehl, H. Clark, and H. H. Williard, *Inorg. Synth.,* **1**, 186 (1939).

(25) S. Kirschner, *Inorg. Synth.,* **5**, 186 (1957).

(26) F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.,* **80**, 4480 (1958).

(27) P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.,* **90**, 1187 (1968).

(28) G. Davies and B. Warnquist, *Coord. Chem. Rev.,* **5**, 349 (1970).

(29) H. Diebler and N. Sutin, *J. Phys. Chem.,* **68**, 174 (1964).

(30) Reference 2e, pp 152–158.

(31) S. D. Malone and J. F. Endicott, *J. Phys. Chem.,* **76**, 2223 (1972).

(32) (a) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.,* **94**, 1797 (1972); (b) G. Ferraudi and J. F. Endicott, *Inorg. Chem.,* **12**, 2389 (1973).

(33) A. T. Thornton and G. S. Laurence, *J. Chem. Soc., Dalton Trans.,* 804 (1973).

(34) A. T. Thornton and G. S. Laurence, *J. Chem. Soc., Dalton Trans.,* 1632 (1973).

(35) W. Waltz and A. W. Adamson, *J. Phys. Chem.,* **73**, 4250 (1969).

(36) H. L. Younmans, "*Statistics for Chemistry*", C. E. Merill Publishing Co., Ohio, 1973.

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

(38) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.,* **79**, 630 (1975).

(39) R. Kyde and W. C. E. Higginson, *J. Chem. Soc.,* 1998 (1960).

(40) Y. Kurimura, I. Meguro, and K. Ohashi, *Bull. Chem. Soc. Jpn.,* **44**, 3367 (1971).

(41) A. Haim and N. Sutin, *J. Am. Chem. Soc.,* **88**, 5343 (1966).

(42) A. Pidcock and W. C. E. Higginson, *J. Chem. Soc.,* 2798 (1963).

(43) For additional details of the NMR studies see Table I and the supplementary material (Figures S1–S4).

(44) (a) T. S. Roche and J. F. Endicott, *J. Am. Chem. Soc.,* **94**, 8622 (1972); (b) *Inorg. Chem.,* **13**, 1575 (1974).

(45) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Am. Chem. Soc.,* **98**, 86 (1976).

(46) R. G. Wilkins, *Acc. Chem. Res.,* **3**, 408 (1970).

(47) Ionic strength corrections have been performed using log $k = Z_A Z_B$ fn(μ),[47] where fn(μ) is an empirical function of ionic strength determined using data from Ru(NH$_3$)$_6$$^{2+}$ reactions of cobalt(III) ammine complexes.[48] For the diffusion-controlled Ru(bpy)$_3$$^{3+}$/Ru(NH$_3$)$_6$$^{2+}$ reaction, the ionic strength correction was based on ref 49.

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

(49) (a) J. F. Endicott and H. Taube, *Inorg. Chem.,* **4**, 437 (1965); (b) R. C. Patel, Ph.D. Dissertation, Boston University, 1969.

(50) J. Holzwarth and H. Jürgensen, *Ber. Bunsenges. Phys. Chem.,* **78**, 526 (1974).

(51) M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem., Soc.,* **99**, 5615 (1977).

(52) G. M. Brown, private communication.

(53) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.,* **11**, 1460 (1972).

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

(55) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.,* **96**, 4710 (1974).

(56) This approximation is reasonable for very similar complexes (e.g., in Co(N$_4$)(OH$_2$)Cl^{2+} + Co(N$_4$)(OH$_2$)$_2$$^{2+}$ reactions) since the second and third terms in (19) should be pairwise matched. It can also be shown that $\Delta G^{\circ}_{12} = \Delta[\Delta H^{\circ}(\text{M-X})] - T\Delta S^{\circ}_{el} - T\Sigma(\Delta S_{Aj} - \Delta S_{Bj}) + g$, where $\Delta H^{\circ}(\text{M-X})$ is the M-X homolysis bond energy, ΔS°_{el} is the standard entropy change associated with the outer-sphere electron-transfer reactions of M-OH$_2$ complexes, the ΔS_{ij} terms are associated with the formation of various five-coordinate species in a simple entropy cycle, and g is a free-energy term due to association of M^{III}L$_5$ and Co^{III}(N$_4$)(OH$_2$)X (J. F. Endicott, J. M. Ciskowski, and C. L. Wong, work in progress). The enthalpy and ΔS°_{el} terms are similar for inner-sphere and outer-sphere reactions (see also J. F. Endicott, *Inorg. Chem.,* **16**, 494 (1977)). Thus the difference between ΔG°_{12} and $\Delta G^{\circ'}_{12}$ would lie largely in the ΔS_{ij} terms; these are expected to be similar for closely related species. The free energy of association, g, should make a nearly constant contribution for species of similar charge type.

(57) K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.,* **11**, 310 (1972).

(58) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.,* **95**, 5539 (1973).

(59) For example, see (a) R. P. Van Duyne and S. F. Fischer, *Chem. Phys.,* **5**, 183 (1974); (b) N. R. Kestner, J. Logan, and J. Jortner, *J. Phys. Chem.,* **78**, 2148 (1974); (c) S. Efrima and M. Bixon, *J. Chem. Phys.,* **64**, 3639 (1976).

(60) P. Hurwitz and K. Kustin, *Trans. Faraday Soc.,* **62**, 427 (1966), found $k_{exch} = 2.3 \times 10^5$ M^{-1} s^{-1} for IrCl$_6$$^{2-,3-}$.

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

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

(63) For a given electron transfer reaction we expect[64]

$$\Delta H^{\ddagger}_{12} = \frac{(\Delta H^{\ddagger}_{11} + \Delta H^{\ddagger}_{22})}{2}(1 - 4\alpha^2) + \frac{\Delta H^{\circ}_{12}}{2}(1 + 4\alpha)$$

where $\alpha = \delta G^{\circ}_{12}/4(\Delta G^{\ddagger}_{11} + \Delta G^{\ddagger}_{22})$. For the corresponding self-exchange reactions, $\delta G^{\ddagger}_{ij} = \lambda_j/4$, where $\lambda_j = (\lambda_i)_j + (\lambda_o)_j$. The terms con-

tributing to $(\lambda_i)_j$ are expected to be mostly enthalpic. If we then consider

$$\Delta H^{\ddagger}_{13} = \frac{(\Delta H^{\ddagger}_{11} + \delta H^{\ddagger}_{33})}{2}(1 - 4[\alpha']^2) + \frac{\Delta H^{\circ}_{13}}{2}(1 + 4\alpha')$$

then $\Delta H^{\ddagger}_{12} - \Delta H^{\ddagger}_{13} \simeq (\Delta H^{\ddagger}_{22} - \Delta H^{\ddagger}_{33})/2$, since $(\alpha - \alpha')$ and $(\alpha^2 - [\alpha']^2)$ are very small ($\sim 10^{-3}$). We further expect that $\Delta(\Delta H^{\ddagger}_{12}) = \Delta H^{\ddagger}_{12} - \Delta H^{\ddagger}_{13} \simeq [(\lambda_i)_2 - (\lambda_i)_3]/8$ since $(\lambda_o)_2 \simeq (\lambda_o)_3$ (the macrocyclic complexes are about the same size and have the same charge).

(64) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975).
(65) Note that for the inner-sphere reactions the Co^{II}–OH$_2$ "bond energies" ($\Delta G^{\circ}_{A_2}$ and $\Delta G^{\circ}_{B_2}$) in Scheme II may not be identical and their difference may contribute to $\Delta(\Delta H^{\ddagger}_{12})$.
(66) In addition to the examples cited here, we have found $\Delta H^{\ddagger} = 49$ kJ mol^{-1} for the Co([14]dieneN$_4$-one)(OH$_2$)$_2^{3+}$/Co([14]tetraeneN$_4$)(OH$_2$)$_2^{2+}$ "exchange" reaction (R. Sriram and J. F. Endicott, unpublished observations), in contrast to the values of $\Delta H^{\ddagger} \simeq 25$ kJ mol^{-1} found for the inner-sphere "exchange" reactions in Table V. This is very nicely consistent with Figure 3 and the conclusion that $\Delta G_i(IS) = 0.5\Delta G_i(OS)$, and once again indicates that the similar ratios of self-exchange rates for outer-sphere and inner-sphere pathways of the [14]tetraeneN$_4$ and [14]dieneN$_4$ systems indicate a relatively large entropic contribution in the inner-sphere reactions of the [14]dieneN$_4$ complexes.
(67) For the first acid hydrolysis steps of Co([14]dieneN$_4$)Cl$_2^+$ and Co([14]tetraene N$_4$)Cl$_2^+$, $\Delta S^{\ddagger} = +51^{18d}$ and -24 kJ mol^{-1} deg^{-1},^{22} respectively. This difference has been attributed to "relaxation of strain" in a dissociative transition state. Similar arguments have been proposed for hydrolyses in a variety of macrocyclic complexes; various aspects of this question have been discussed in ref 12, 18d, 68, and 69. Macrocyclic complexes with asymmetric axial ligation do not consistently exhibit variations in $\Delta S^{\ddagger}$, perhaps owing to differences in stability of isomeric species. However,
(68) homolyses of Co([14]diene N$_4$)OH$_2$X^{2+} complexes have strongly implicated a large entropy term associated with formation of five-coordinate intermediate species (J. F. Endicott, J. M. Ciskowski, and C. L. Wong, work in progress; see also footnote 56).
(68) C. K. Poon, *Coord. Chem. Rev.*, **10**, 1 (1973).
(69) Y. Hung and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 4977 (1977).
(70) Based on eq 1, $k_{AB} = (k_{AA}k_{BB}K_{AB})^{1/2}$ and $k_{BA} = (k_{BB}k_{AA}K_{BA})^{1/2}$ since ΔG°_{AB} is small for these reactions.
(71) There is a small ambiguity in the location of the intercept. In Figure 3 we have assumed that K'_{OS} for the Co(N$_4$)(OH$_2$)$_2^{3+,2+}$ reactions (at $\mu = 1.0$) is approximately equal to $K_{OS}k_C$ for the Co(N$_4$)(OH$_2$)Cl^{2+}/Co(N$_4$)(OH$_2$)$_2^{2+}$ reactions (at $\mu = 0.1$). A better estimate might be $5K'_{OS} \sim K_{OS}k_C$ (see Table VI) leading to a discrepancy of about 5 kJ mol^{-1} in the location of zero on the abscissa. Equilibria are as defined in Scheme I.
(72) This is plausible since there is only a small change in dipole moment within the very bulky inner-sphere precursor complex. Of course this is also expected when (as here) $(a + b) > r$ in eq 21, using

$$\lambda_o = e^2\left(\frac{1}{2a} + \frac{1}{2b} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)$$

(see ref 2c–f and 3). D_{op} and D_s are the optical and static dielectric constants of the aqueous medium (see ref 3). A probably more accurate and even smaller value of λ_o may be obtained using an ellipsoidal model of the interpenetrating spheres of the inner-sphere precursor complex: R. D. Cannon, *Chem. Phys. Lett.*, **49**, 299 (1977). Unfortunately r is not an easily estimated parameter in the inner-sphere systems we have examined.
(73) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 118 (1960).
(74) J. A. Stritar and H. Taube, *Inorg. Chem.*, **8**, 2281 (1969).
(75) A. G. Sykes, "Kinetics of Inorganic Reactions", Pergamon Press, Oxford, 1966, pp 183–188.

Reaction of a Tetraaza[14]annulene Cobalt(III) Complex with Acetylene. Synthesis and Structural Characterization of a Novel Cobalt(III) Complex Containing a Pentadentate Macrocyclic Ligand with a Carbon σ-Donor Atom: [(7-(*cis*-β-Vinylide)-7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecinato)pyridinecobalt(III)] Hexafluorophosphate Monoacetonitrile

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Abstract: The cycloaddition reaction of acetylene with Co(III) complexes of the 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecinato ligand yields a novel, dianionic pentadentate macrocycle with four equatorial nitrogen donor atoms and a vinylide carbon σ donor occupying one axial site. The Co(III) complex containing this ligand, [Co(C$_{24}$H$_{24}$N$_4$)(C$_5$H$_5$N)]PF$_6$·CH$_3$CN, crystallizes in the monoclinic space group *Pc* with cell parameters $a = 10.644$ (2) Å, $b = 8.309$ (2) Å, $c = 18.614$ (5) Å, $\beta = 107.7$ (1)°, and $Z = 2$. The structure was refined by Fourier and least-squares techniques to conventional and weighted *R* values of 4.1 and 4.7%, respectively, based on 4490 unique data with $|F_o| \geq 3\sigma|F_o|$. The acetylene has added across one six-membered 2,4-pentanediiminato chelate ring bridging the cobalt atom and the methine carbon. The resultant macrocycle contains a bicyclic, tridentate chelate with pentane-2,4-diimine-3-vinylide functionalities and an unmodified 2,4-pentanediiminato chelate ring. The Co(III) atom lies in the N$_4$ donor atom plane with an average Co–N distance of 1.892 Å. The Co–C(vinylide) distance is 1.908 Å. The long Co–N(pyridine) distance of 2.098 Å is attributable to a combination of a trans effect and steric interactions. The importance of peripheral steric interactions within the ligand on the details of the macrocyclic ligand conformation and the role these play in the formation of the complex are discussed. Structural comparisons are made with other Co(III)–vinyl species and with Co(III) porphyrin complexes.

Introduction

The reactions of cobalt macrocyclic systems have aroused interest because of their ability to model phenomena in biologic systems. The activation of carbon-containing compounds for isomerization and alkyl-transfer reactions is known to occur in situ in the biosphere and has been modeled in various coenzyme B$_{12}$ analogue species.$^{2-4}$ Consequently structural studies of unsaturated macrocyclic systems have proven to be

informative and to sometimes yield important results. The most notable case, was the full structural characterization of vitamin B$_{12}$ by Lenhert and Crowfoot-Hodgkin.^{5} This elucidation of a naturally occurring, stable Co–C bonded species prompted the search for related synthetic organotransition metal complexes.

Synthetic schemes attempting to model B$_{12}$ behavior have resulted in novel structures and reactions. For example, the