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Oxidation-Reduction Reactions with Macrocyclic Ligands. Dependence of the Rate Advantage for the Inner-Sphere Electron-Transfer Pathway on Electronic Structure for Low-Spin $Co^{\mathrm{III,II}}$, $Ni^{\mathrm{III,II}}$, and $Cu^{\mathrm{III,II}}$ Couples[1]

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Abstract: Simple electron-transfer reactions involving $Ni^{\mathrm{III,II}}(N_4)$ and $Cu^{\mathrm{III,II}}(N_4)$ couples have been examined and compared in relative rates to reactions of $Co^{\mathrm{III,II}}(N_4)$ and $Fe(OH_2)_6^{3+,2+}$ couples (N_4, a tetraaza-macrocyclic ligand). These couples provide a relatively systematic variation in metal ion electronic structure and permit an evaluation of the dependence of electron-transfer rates on reactant electronic configurations. Outer-sphere cross-reactions and redox potentials of the couples have been used to estimate the range of self-exchange rate constants for the $M^{\mathrm{III,II}}(N_4)$ complex. These are $10^{5\pm1}$ and $10-10^4$ $M^{-1}\ s^{-1}$ for M = Cu and Ni, respectively. These relatively facile exchange rates may be contrasted to 10^{-1} to 10^{-5} $M^{-1}\ s^{-1}$ for M = Co, and the ranges and variations are readily explained in terms of differences in ground-state structural parameters and the resulting first coordination sphere reorganizational energies. No additional specific role for the differences in electronic structure could be found in outer-sphere reactions. In contrast, Cl^--bridged, inner-sphere reactivity patterns were found to vary dramatically with reactant electronic structure. The kinetic advantage of the inner-sphere pathway has been defined in terms of the ratio of rate constants for bimolecular inner-sphere and the equivalent outer-sphere reactions. For example, rates of $Co(OH_2)_5Cl^{2+}$ and $Co(OH_2)_6^{3+}$ oxidations of $M^{\mathrm{II}}(N_4)$ complexes may be taken as approximate measures of the appropriate parameters, and the ratio of these rates, $k^{\mathrm{IS}}/k^{\mathrm{OS}}$, serves as an index of the kinetic advantage of the inner-sphere pathway for the various complexes. Other comparisons have employed $M^{\mathrm{III}}(N_4)Cl$ oxidants or $Fe(OH_2)_6^{2+}$ substrates. Values of $k^{\mathrm{IS}}/k^{\mathrm{OS}} \simeq 10^{6\pm1}, 10^{5\pm1}, \sim 2, \sim 10^4$, and $\sim 10^{2.2}$, respectively, for $Co^{\mathrm{III}}/Co^{\mathrm{II}}$, $Co^{\mathrm{III}}/Ni^{\mathrm{II}}$, $Co^{\mathrm{III}}/Cu^{\mathrm{II}}$, $Co^{\mathrm{III}}/Fe^{\mathrm{II}}$, and $Ni^{\mathrm{III}}/Ni^{\mathrm{II}}$ reactions. These variations in reactivity are rationalized in terms of a three-center (M-Cl-M) transition-state-bonding interaction. It is proposed that the inner-sphere pathway becomes more effective as the number of electrons in the 3-center system decreases, with 3- and 4-electron configurations resulting in reasonably stable transition states and the 5-electron configuration destabilizing the interaction. It is also concluded that the bridging pathway is only effective if the 3-center-bonding interaction effectively mixes the electron-transfer donor and acceptor orbitals; this feature is discussed in terms of symmetry constraints and surface-crossing restrictions.

The dependence of reaction rates upon reactant electronic configurations is a fundamental concern in systematic discussions of chemical reactivity. However, the reactivity patterns found in the simplest class of oxidation-reduction reactions of transition-metal complexes, viz., outer-sphere electron-transfer processes, can be largely[2-10] (but not entirely[9-13]) attributed to the changes in nuclear position that accompany electron transfer. Consequently, the models used to describe the reaction coordinate in such systems employ Born-Oppenheimer potential energy surfaces for the reactant and product "states", and the electronic contribution is treated as a perturbation coupling the Born-Oppenheimer surfaces at their intersection point.[2-10,14,15] Related models for more complex oxidation-reduction reactions are much more primitive. In the simplest of these reactions, those which couple transfer of a bridging ligand to the electron-transfer process,[2,16,17]

$$L_5M^{\mathrm{III}}-X + M'^{\mathrm{II}}S_6 \rightarrow L_5M^{\mathrm{II}}S + S_5M'^{\mathrm{III}}-X \qquad (1)$$

(for S a solvent species), it has been frequently postulated that such purely electronic factors as donor-acceptor orbital symmetry should play a major role in determining reactivity patterns.[2,16-22] Such a major role for electronic factors should lead to a very different model for inner-sphere and for outer-sphere electron-transfer reactions.

In fact there is reason to believe that Franck-Condon factors still contribute significantly to inner-sphere electron-transfer reactions,[23,24] and that, at least to some degree, Born-Oppenheimer

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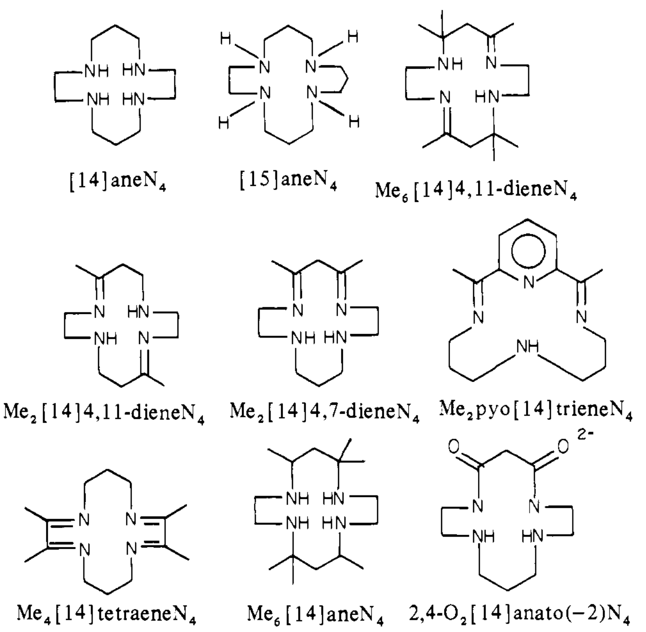
potential energy surfaces could be a useful starting place for descriptions of the reaction coordinate.[2,24-26] It is pertinent that this kind of approach has received increasing attention in systematic descriptions of many related types of group-transfer reactions.[24b,c,25-32]

Unfortunately, much of the earlier work on inner-sphere electron-transfer reactions involved systems with unknown equilibrium constants K_1, as when product species equilibrate very rapidly with the solvent ($L_5M^{II}S + 5S \rightarrow M^{II}S_6 + 5L$). Thus, it is rare that the intrinsic (free-energy independent) barriers have been distinguished in the reactivity patterns. Nevertheless, correlations between inner-sphere and outer-sphere reactivity patterns[2,17,24a,24d] demonstrate that Franck–Condon factors do contribute to the inner-sphere pathway and ensure that the reaction rates will be free-energy dependent.[24-26,31] In order to progress in the understanding of such complex reactions, it is necessary to obtain free-energy-independent reactivity patterns. This is especially important in any search for the effects of factors that are electronic in origin, since electronic factors are not dependent on the reactant–product energy gap.

The traditional approach to the bridging ligand dependence of inner-sphere reaction patterns emphasizes the substitutional nature of the reaction by postulating the intermediacy of metastable "precursor" (e.g., L_5M^{II}-X-$M'^{III}S_5$) complexes,[2,16,17,20,21,24a,33,34] in which it is at least implicit that the electrons are valence trapped at the individual metal centers and that bond breaking/making processes occur independent of electron transfer. In this approach, in the limit that precursor complex formation is not rate limiting, the reaction rate is often discussed in terms of variations in stability of these precursor complexes, e.g., as $k_{obsd} \simeq K_p k_e^p$, where K_p is an equilibrium constant for precursor complex formation and k_e^p is the electron transfer rate in the precursor complex. In our view, this approach suffers from a number of difficulties: (1) it overemphasizes a heterolytic reaction coordinate; (2) if metastable (or valence trapped) intermediates do not exist the partitioning of the rate constant ($k_{obsd} \simeq K_p k_e^p$) is not likely to lead to useful models; (3) the orbitals involved in bonding in the "precursor complex" in the systems of concern here are the same orbitals that are involved in electron transfer and this makes the whole description internally inconsistent; and, (4) the "precursor complex" formulation does not provide any useful insight into reactions in which alkyl groups function as "bridging ligands".[24b,c,35,36] There is a very limited amount of X-ray structural work pertinent to Co^{III}-X-M interactions; thus, the Co–S bond in $\{((en)_2Co(SCH_2CH_2NH_2))(Cu(CH_3CN)_2)\}_2^{6+}$[37] is about 3 pm longer than the Co–S bond in $((en)_2Co(SCH_2COO))_2Ag^{3+}$.[38] Since the Cu(I)/Co(III) electron transfer proceeds at a measurable rate,[37] the slightly longer bond in this complex is suggestive of appreciable donor–acceptor mixing (or electron delocalization) in the precursor complex; the small difference in bond lengths observed in these complexes is consistent with the very small value expected for the electron transfer ($Cu^I \rightarrow Co^{III}$) equilibrium constant.

Chart I



We have been considering approaches in which the inner-sphere reaction coordinate can be described in terms of simple ground-state properties of the reactant complexes. We consider only those reactions for which metal–ligand heterolysis on the labile partner is not rate limiting. Under these circumstances, the probability of an encounter appropriate to the inner-sphere pathway is proportional to K_0K_w (K_0 is the outer-sphere association constant; K_w is the equilibrium constant for M^{II}–OH_2 dissociation), and $k_{obsd} \simeq K_0K_wk_e$. This approach has led us to propose[24a-c] some features which should be important in a model for the intrinsic barrier to coupled bridging ligand–electron transfer reactions: (a) a homolytic reaction coordinate for k_e (to account for anharmonicities and because the M^{III}-X^- bond breaking is homolytic); (b) a reorganizational barrier resulting from any changes in bond length, angles, etc.; and (c) a three-center transition-state-bonding interaction, mediated by the bridging ligand. For sufficiently strong transition-state bonding, the three-center bond should have the effect of reducing the Franck–Condon barrier. This approach is useful for both alkyl- and halide-bridged electron-transfer reactions,[24b,c] and it incorporates general features found in the models and concepts proposed previously by Halpern and Orgel,[18b] Burdett,[22] and Cannon.[2,39] It is also closely related to several models of nucleophilic-displacement, group-transfer, or atom-transfer reactions.[25-32] A unique feature of the model which we have evolved is our description of the transition-state donor–acceptor interactions in terms of a 3-center bond. There are a number of qualitative features of 3-center bonding interactions that should be amenable to experimental investigation.

The present study was designed to explore the response of electron-transfer reactivity patterns to stepwise changes in the reactant d-electron configurations. Among the couples compared in this study, the electron-transfer donor orbital is varied in occupation (d_{z^2} or $d_{z^2}{}^2$) or symmetry (d_{z^2}, $d_{x^2-y^2}$ or d_{xz}, d_{yz}). Since the macrocyclic ligands that we have employed restrict any

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bridging-ligand electron-transfer pathway to the axial coordination positions, these simple changes in electron configuration might have a profound influence on reactivity patterns,

Experimental

Reagents, Most of the cobalt, nickel, and copper macrocyclic complexes were prepared as given in the literature.[10,24,40-42] $Cu^{II}([14]aneN_4)$[43] was prepared by adding $Cu(ClO_4)_2{\cdot}6H_2O$ to a solution of $[14]aneN_4$ in ethanol and recrystallized from hot water, Anal: Calcd. for $C_{10}H_{24}N_4O_8Cl_2Cu$: C, 25.95; H, 5.23; N, 12.11; Cl, 15.32. Found: C, 26.54; H, 5.62; N, 12.33; Cl, 15.31. The $2,4\text{-}O_2[14]\text{-anato}(-2)N_4$ ligand was prepared as described in ref 44. The copper complex was prepared by adding an equimolar amount of $Cu(CH_3COO)_2{\cdot}H_2O$ to a hot solution of ligand in water. $Ni^{II}(Me_4[14]tetraeneN_4)$ was prepared by the literature method, but we found purification difficult. To purify $(Ni(Me_4[14]tetraeneN_4))(ZnCl_4)$, prepared as described in ref 42, a column was prepared with DOWEX 50W-X4, 100–200 mesh cation exchange resin in the H^+ form. A 100-mL solution approximately 0.1 M in $(Ni(Me_4[14]tetraeneN_4))(ZnCl_4)$ was used to load the column. The loaded column was washed with distilled water and 0.1 M and finally 0.2 M $HClO_4$ until the effluent was free of Cl^-. The nickel complex was eluted with 2 M $HClO_4$ and the eluent solution concentrated on a rotary evaporator. Addition of a mixture of ethanol and ether precipitated the complex. The precipitate was dried and then recrystallized from dilute $HClO_4$.

The $Cu^{II}(Me_4[14]tetraeneN_4)$ complex was isolated as the PF_6^- salt of the imidazole adduct from a synthesis similar to that reported for $Fe^{III}(Me_4[14]tetraeneN_4)$.[45] The perchlorate salt was obtained by recrystallization from 1 M $HClO_4$.

Warning: The perchlorate salts used in this study are explosive and potentially hazardous.

All the solutions for kinetic studies were prepared with water distilled in a Corning-Mega Pure still. The perchlorate solutions of $Fe(phen)_3^{3+}$ and $Ru(bpy)_3^{3+}$ were obtained fresh for each determination by PbO_2 oxidation of the divalent metal complexes in $HClO_4$. Solutions of $Co(OH_2)_6^{3+}$ were prepared by electrolysis of $Co(ClO_4)_2{\cdot}xH_2O$ in 3 M $HClO_4$ at 0 °C;[46] $[Co(OH_2)_6^{3+}]$ was determined from the absorbances of stock solutions at 605 nm (ϵ 35 $M^{-1}\ cm^{-1}$).[46] Solutions of $Ni^{III}(N_4)$ complexes were obtained by PbO_2 or Ce^{IV} oxidations of acidic solutions of the corresponding $Ni^{II}(N_4)$ complexes. The conversion of Ni(II) to Ni(III) was confirmed from the product spectra. Solutions of reducing agents were deaerated by purging with a stream of Cr^{2+}-scrubbed N_2 or Ar. The solutions of $Ni^{III}(Me_4[14]tetraeneN_4)$ and $Ni^{III}(Me_6[14]4,11\text{-}dieneN_4)$ were used within 30 min of preparation.

Electrochemistry, Half-wave potentials were determined by cyclic voltammetry on a Princeton Applied Research Model 173 Potentiostat and a Model 175 Universal Programmer. All electrochemical studies were done in 1–6 M $HClO_4$. Solutions were deaerated with Cr^{2+}-scrubbed, purified N_2. Most of the studies employed a Pt working electrode and a NaCl–calomel reference electrode.

Kinetic Techniques, Kinetic studies of thermal reactions were made with an Aminco stopped flow instrument that was thermostated at the desired temperature. All reactions were run under pseudo-first-order conditions with either reductant or oxidant in large excess. Most reactions involved small changes of absorbance, and values of k_{obsd} were calculated from either log $(T_\infty - T_t)$ vs. time plots or reaction half-lives. Pseudo-first-order plots were linear for about 90% of the reaction. Second-order rate constants were calculated from the slope of k_{obsd} vs. concentration of excess reagent by least-squares analysis.

Photochemical Generation of Cl_2^- and $Co(OH_2)_5Cl^{2+}$, These oxidants were generated in situ by using flash photolysis techniques described previously.[24a,47,48] (a) Cl_2^- was generated by flash photolysis (xenon flash; sample cell jacket containing a UV cut-off filter such as 0.015 M toluene in hexane) of $Co(NH_3)_5Cl^{2+}$ in HCl; (b) $Co(OH_2)_5Cl^{2+}$ was generated by flash photolysis of $Co(NH_3)_5Cl^{2+}$ in HCl and Co^{2+}. $Co(ClO_4)_2$ was prepared by dissolving high-purity Co metal (99.999%) in $HClO_4$. By adjusting reactant concentrations, any of the thermal reactions subsequent to irradiation may be observed.

$$5H^+ + Co(NH_3)_5Cl^{2+} + h_\nu \xrightarrow{H_2O} Co(OH_2)_6{}^{2+} + 5NH_4{}^+ + {\cdot}Cl \tag{2}$$

$${\cdot}Cl + Cl^- \rightleftarrows Cl_2^-$$

$$Cl_2^- + Co(OH_2)_6{}^{2+} \xrightarrow[H_2O]{} Co(OH_2)_5Cl^{2+} + Cl^- \tag{3}$$

$$Cl_2^- + M(N_4)^{2+} \rightarrow Cl\text{–}M(N_4)^{2+} + Cl^- \tag{4}$$

$$Co(OH_2)_5Cl^{2+} + M(N_4)^{2+} \rightarrow Cl\text{-}M(N_4)^{2+} + Co(OH_2)_6{}^{2+} \tag{5}$$

In the present experiments, transient transmittance changes generated from the flash photolysis apparatus have been stored in a Nicolet Explorer III digital oscilloscope and subsequently analyzed by using local variations of standard least-squares programs.

The jacket of the flash photolysis cell was filled with 0.015 M toluene in hexane when $Co(NH_3)_5Cl^{2+}$ or $Co(Me_4[14]tetraeneN_4)(OH_2)Cl^{2+}$ were used to generate Cl_2^-. The jacket contained 0.015 M naphthalene in hexane when $FeCl^{2+}$ was used to generate Cl_2^-. In these experiments, $[Co(NH_3)_5Cl^{2+}]$ was usually 5×10^{-5} M; $[Co^{2+}] = 0.1$ M; $[M(N_4)^{2+}] = (0.08\text{-}2) \times 10^{-4}$ M; $[Cl^-] = 0.01\text{-}1$ M, $\mu = 1.0$ M ($HClO_4$).

Results

A, Electrochemistry, The pertinent electrochemical data are presented in Table I, The cyclic voltammograms were obtained in 2×10^{-3} M solutions of the nickel(II) and/or copper(II) complexes which were strongly acidic. It has been our experience that the aqueous stability of the respective $M^{III}(N_4)$ complexes decreases rapidly as pH increases. Most of these voltammograms were quasireversible, with 60–100-mV separations of the anodic and cathodic peaks, and the oxidations occurred at relatively high potentials (Table S-I).[49] While most of the $Ni^{III,II}(N_4)$ couples were reasonably well behaved, there was a significant difference in cathodic and anodic peak amplitudes for the $Ni^{III,II}(Me_2[14]\text{-}4,7\text{-}dieneN_4)$ couple even in strong acid; this system apparently involves ligand oxidation and is discussed in detail elsewhere,[50] The potential for the $Ni^{III,II}([14]aneN_4)$ couple becomes smaller in chloride media. This shift in potential is in accord with the relatively strong axial coordination of anionic ligands frequently observed for $Ni^{III}(N_4)$ complexes,[51-53] and implies large association constants for $Ni^{III}([14]aneN_4)$ and Cl^-, qualitatively as reported by Haines and McAuley.[54] We did not detect any such pronounced variation of potential with (Cl^-) for any other $Ni^{III,II}$ couples since the onset of Cl^- oxidation obscures much of the high-potential region,

The $Cu^{III,II}(N_4)$ couples were electrochemically more complex. In general, the $Cu^{III}(N_4)$ complexes are stronger oxidants and have shorter lifetimes than the corresponding $Ni^{III}(N_4)$ complexes. The best behaved copper system in our hands was the $Cu^{III,II}(Me_6[14]4,11\text{-}dieneN_4)$ couple for which we observed a good quality, nearly reversible voltammogram with $E_{1/2} = 1{,}16$ V vs. SCE (ΔE_p

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(43) Abb: $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecaneN$_4$; $Me_6[14]\text{-}4,11\text{-}dieneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dieneN$_4$; $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraeneN$_4$; $Me_2pyo[14]trieneN_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadeca-1(17),2,11,13,15-pentaneN$_4$; $Me_2[14]4,11\text{-}dieneN_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dieneN$_4$; $Me_6[14]aneN_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane; $Me_2[14]\text{-}4,7\text{-}dieneN_4$ = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene.

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Table I. Summary of Kinetic Data for Outer-Sphere Electron-Transfer Reactions of $Ni(N_4)$ and $Cu(N_4)$ Complexes (25 °C)

oxidant	reductant[a]	10^4[Ox], M	10^4[Red], M	medium	k, M^{-1} s^{-1}
$Fe(phen)_3{}^{3+}$	$Ni^{II}L(1)$	0.3-1.0	0.10	1.5 M $HClO_4$	1.6×10^6
$Fe(dmpy)_3{}^{3+}$	$Ni^{II}L(1)$			1 M TPSA[b]	2.9×10^5 [c]
$Fe(dmph)_3{}^{3+}$	$Ni^{II}L(1)$			1 M TPSA[b]	5.7×10^5 [c]
$Co(OH_2)_6{}^{3+}$	$Ni^{II}L(1)$	2-27	0.16	1.5 M $MClO_4$ ($M = H^+, Li^+$)	86[d]
	$Ni^{II}L(2)$	17-85	1.0	1.5 M $MClO_4$ ($M = H^+, Na^+$)	60[d,e]
	$Ni^{II}L(3)$	23-230	1.0	1.5 M $MClO_4$ ($M = H^+, Li^+$)	50[d]
	$Ni^{II}L(6)$	13-38	1.0	3.0 M $HClO_4$	750
	$Ni^{II}L(4)$	6.3-50	1.0	3.0 M $HClO_4$	947
	$Cu^{II}L(1)$	20-80	1.0	1.5 M $HClO_4$	2.8×10^3
	$Cu^{II}L(2)$ (racemic)	25-75	5.0	3.0 M $HClO_4$	1.0×10^2
	$Cu^{II}L(2)$ (meso)	20-75	4.0	3.0 M $HClO_4$	1.0×10^2
$Ru(bpy)_3{}^{3+}$	$Ni^{II}L(2)$	1-5	0.10	0.1 M $HClO_4$	1.4×10^3
	$Ni^{II}L(3)$	0.5-20	0.10	0.1 M $HClO_4$	7.8×10^5
	$Ni^{II}L(6)$	0.10	0.25-1.0	1.0 M $HClO_4$	3.3×10^6
$Ni^{III}L(1)$	$Co^{II}L(1)$	0.50	2.3-5.0	1.5 M $HClO_4$	2.3×10^4
	$Co^{II}L(2)$	0.50	10-50	1.5 M $HClO_4$	7.6×10^2
	$Co^{II}L(3)$	0.50	1.3-15	1.5 M $HClO_4$	4.6×10^4
	$Co^{II}L(4)$	1-10	0.55	1.5 M $HClO_4$	1.3×10^5
$Ni^{III}L(2)$	$Co^{II}L(1)$	0.50	2-10	1.5 M $HClO_4$	2.0×10^5
	$Co^{II}L(2)$	0.50	2.5-25	1.5 M $HClO_4$	2.8×10^3
	$Co^{II}L(3)$	6.3-25	1.0	1.5 M $HClO_4$	3.1×10^4
	$Co^{II}L(4)$	2.5-10	0.91	1.5 M $HClO_4$	9.5×10^3
	$Co^{II}L(5)$	0.50	1-10	1.5 M $HClO_4$	1.5×10^4
	$Ru(bpy)_3{}^{2+}$	1.3-7.5	0.10	1.0 M $HClO_4$	2.7×10^4
$Ni^{III}L(3)$	$Co^{II}L(2)$	1.0	5-20	3.0 M $HClO_4$	2.1×10^4
$Ni^{III}L(6)$	$Ni^{II}L(1)$	0.50	3-20	1.0 M $HClO_4$ and 1.0 M $NaClO_4$	1.9×10^3
	$Co^{II}L(2)$	0.25	5.25	1.0 M $HClO_4$	2.0×10^2
	$Co^{II}L(3)$	1.2-5	0.50		1.4×10^4
	$Co^{II}L(4)$	2.5-12	1.0		3.1×10^4

[a] L(1) = [14]aneN_4; L(2) = Me_6[14]4,11-dieneN_4; L(3) = Me_4[14]tetraeneN_4; L(4) = Me_2pyo[14]trieneN_4; L(5) = [15]aneN_4; L(6) = Me_2[14]4,11-dieneN_4. [b] Toluenesulfonic acid. [c] Reference 56a. [d] Rate constant obtained by extrapolating $k_{obsd} = k_I + k_{II}'/[H^+]$ to $[H^+]^- = 0$. [e] Activity correction used in evaluation based on the following: Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions"; Reinhold Publishing Co.: New York, 1958; pp 597-599.

= 60 mV). This may be compared to $E_{1/2}$ = 1.22 V vs. SCE reported for the same complex in acetonitrile.[55] Voltammograms of the remaining complexes exhibited only an oxidation wave ($E_{p,a}$ in the range 1.1-1.3 vs. SCE), consistent with rapid decomposition of the $Cu^{III}(N_4)$ product.

B. Absorption Spectra and Formation Constants for $M^{III}(N_4)Cl$ Species. Figure 1 summarizes the absorption spectra of transient species which result from Cl_2^- (or $Co(OH_2)_5Cl^{2+}$) oxidations of $Ni^{II}(N_4)$ and $Cu^{II}(N_4)$ complexes. The $Ni^{III}(N_4)Cl$ products were generally slow to equilibrate for N_4 = [14]aneN_4, Me_2[14]4,7-dieneN_4, and Me_4[14]tetraeneN_4 ($\tau_{eq} > 1$ ms) under conditions of our experiments, while Ni^{III}(Me_6[14]4,11-dieneN_4)Cl was always at equilibrium with the medium over the duration of flash photolysis experiments ($\tau_{eq} < 60$ μs). Equilibration of Ni^{III}([14]aneN_4)Cl could be observed on long time scales and appeared consistent with literature reports.[54,56]

The $Cu^{III}(N_4)$ complexes were always significantly shorter lived than the corresponding $Ni^{III}(N_4)$ complexes; however, the lifetimes of many of these species are greater than 0.1 ms and adequate for the kinetic studies described. Both spectroscopic and kinetic data imply that the interactions of $Cu^{III}(N_4)$ complexes with Cl^- are weak. Of course, one expects only very weak axial association of solvent or anionic species for low-spin d^8-$M(N_4)$ complexes (weak at least in comparison to the electron-pairing energy).[57,58] It is not important for our immediate purposes whether these axial interactions are labeled "ion-pair", "solvation", or "weak-bonding" interactions. Since the interactions are so weak, replacement of the axial species will generally be more rapid than one finds for the low-spin (d^7) $Co^{II}(N_4)$ analogues.[33,59] As far as we could ascertain, the Cu(III) complexes were always at equilibrium with the solution environment during our experiments.

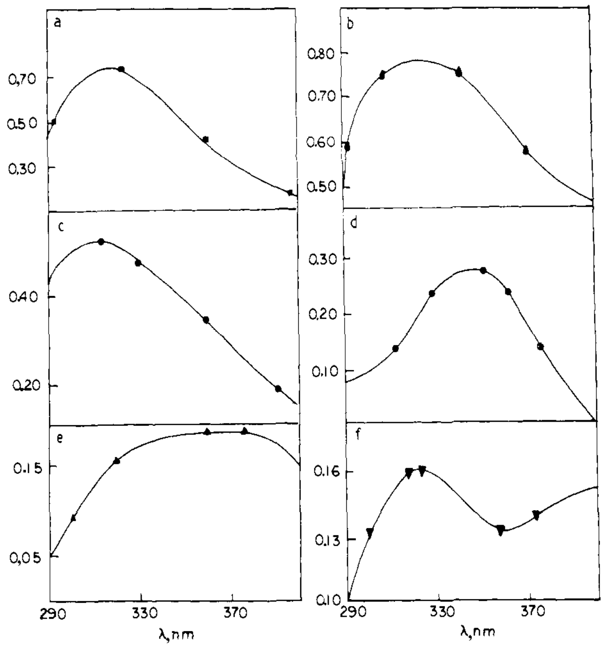

Figure 1. Product spectra for Cl_2^- and $Co(OH_2)_5Cl^{2+}$ oxidations of $Ni^{II}(N_4)$ and $Cu^{II}(N_4)$. All spectra in 1 M HCl, containing 10^{-5} M $M^{II}(N_4)$ and $1\text{-}10) \times 10^{-5}$ M $Co(NH_3)_5Cl^{2+}$: (a) Ni^{III}([14]aneN_4)Cl (7.5 ms after flash); (b) Ni^{III}(Me_6[14]4,11-dieneN_4)Cl (1.5 ms after flash); (c) Ni^{III}(Me_2[14]4,7-dieneN_4)Cl (3.5 ms after flash); (d) Ni^{III}(Me_4[14]tetraeneN_4)Cl (200 μs after flash); (e) Cu^{III}([14]aneN_4) (from Cl_2^- reaction only; 300 μs after flash); (f) Cu^{III}(Me_6[14]4,11-dieneN_4) (from Cl_2^- reaction only; 2.1 ms after flash). Optical densities in the flash photolysis experiments refer to a 20-cm path length.

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(57) Very recently Hunt and co-workers[58] have found that the rate of axial substitution coupled to spin change in Ni^{II}([14]aneN_4), $^1(Ni([14]aneN_4)^{2+})$ + $H_2O \rightleftarrows {}^3(Ni([14]aneN_4)(OH_2)^{2+})$, is 2×10^7 s^{-1}. This is clearly a lower limit on the rate at which nearest neighbor solvent is displaced from the axial region without a change in spin multiplicity.

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Table II, Kinetic Parameters for Formation and Decomposition of $M^{III}(N_4)$ Complexes

		formation		decomposition[a]	
oxidant	reductant	k_5, $M^{-1}\ s^{-1}$	$K_{IP}k_5'$, $M^{-2}\ s^{-1}$	k, s^{-1}	k', $M^{-1}\ s^{-1}$
$Co(OH_2)_5Cl^{2+}$ [b]	$Ni^{II}([14]aneN_4)$	$(5.3 \pm 0.6) \times 10^7$	$(8.4 \pm 1.1) \times 10^7$		
	$Ni^{II}(Me_6[14]4,11\text{-diene}N_4)$	$(7.9 \pm 0.7) \times 10^5$	$(2,1 \pm 0.1) \times 10^6$		
	$Ni^{II}(Me_2[14]4,7\text{-diene}N_4)$	$(1.2 \pm 0.5) \times 10^7$	$(3.9 \pm 0,8) \times 10^7$		
	$Ni^{II}(Me_4[14]\text{tetraene}N_4)$	$(1.6 \pm 0,4) \times 10^5$	$(1.7 \pm 0.3) \times 10^5$		
	$Cu^{II}([14]aneN_4)$	$(4.5 \pm 4,0) \times 10^3$	$(1.09 \pm 0.07) \times 10^5$		
	$Fe(OH_2)_6^{2+}$	$(1.0 \pm 0.4) \times 10^4$	$(5.0 \pm 0.6) \times 10^4$		
Cl_2^-	$Cu^{II}([14]aneN_4)$[c]	$(137 \pm 4) \times 10^7$	$(30 \pm 5) \times 10^7$	6.1 ± 0.3	
	$Cu^{II}(\textit{meso}\text{-}Me_6[14]4,11\text{-diene}N_4)$	$(15 \pm 1) \times 10^7$		0.36 ± 0.03	0.63 ± 0.04
	$Cu^{II}(Me_4[14]\text{tetraene}N_4)$[c]	$(1.9 \pm 0.4) \times 10^7$	$(2.5 \pm 0.7) \times 10^7$	($t_{1/2} \leqslant 60\ \mu s$)	
	$Ni^{II}(Me_6[14]aneN_4)$[d]	2.0×10^9			
	$Ni^{II}(Me_6[14]4,11\text{-diene}N_4)$[d]	9.6×10^9			
	$Ni^{II}(Me_6[14]1,4,8,11\text{-tetraene}N_4)$[d]	8.7×10^9			
	$Co^{II}(Me_6[14]4,11\text{-diene}N_4)$[e]	1.0×10^9			

[a] Rate laws of the form $k_{obsd} = k + k'[Cl^-]$. [b] 25 ± 1 °C; 1 M H^+; 5×10^{-5} M $Co(NH_3)_5Cl^{2+}$; 0.9 M $\geqslant [Cl^-] \geqslant$ 0.01 M (perchlorate media). Most transient absorbance changes observed at 344 nm. Data fitted to eq 6. [c] Rate laws of the form $k_{obsd} = k_5 + K_{IP}k_5'[Cl^-]$. No entry for k_4' means that no chloride dependence has been observed $(k'/k) \leqslant 0,05$ in our work. 1.0 M $HClO_4$, 25 ± 1 °C; $\sim 10^5$ M $Co(NH_3)_5Cl^{2+}$ or $FeCl^{2+}$ (see text). [d] Reference 52. [e] Reference 47a.

For some of the comparisons developed below, it was necessary to know formation constants for some $Co(N_4)(OH_2)Cl^{2+}$ complexes. As a matter of convenience we have examined the first-order approach to equilibrium of $Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{3+}$ in 1.0 M $HClO_4$ with 0,013 M $\leq [Cl^-] <$ 0,208 M, Guggenheim plots[60] were linear over 2.5 half-lives. The observed rate law was $k_{obsd} = k_f[Cl^-] + k_d$, $k_f = (4.0 \pm 0,4) \times 10^{-4}\ M^{-1}\ s^{-1}$, and $k_d = (3.9 \pm 0.4) \times 10^{-5}\ s^{-1}$. Thus, $K_f = k_f/k_d = 10.3 \pm 1.6\ M^{-1}$. The kinetic data are summarized in Table S-II,[49]

The equilibrium constant for

$$\begin{aligned} &Co(Me_4[14]\text{tetraene}N_4)(OH_2)Cl^{2+} + \\ &\qquad Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+} \rightleftarrows \\ &\qquad Co(Me_4[14]\text{tetraene}N_4)(OH_2)_2^{2+} + \\ &\qquad\qquad (OH_2)Cl^{2+}Co(Me_6[14]4,11\text{-diene}N_4) \end{aligned}$$

has been determined to be 0,36 ± 0.04,[24a] This equilibrium constant may be re-expressed as

$$K^{IS} = K^{OS}K_f(K'_f)^{-1}$$

where $k^{OS} = 1.0$ is the equilibrium constant for outer-sphere electron transfer between the diaquo complexes,[10d] and K'_f is the formation constant for $Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)Cl^{2+}$, $K'_f = 29 \pm 5\ M^{-1}$.

C, Outer-Sphere Electron-Transfer Reactions; Oxidations of $Ni^{II}(N_4)$ Complexes, Kinetic data for oxidations with $Co(OH_2)_6^{3+}$, $Ru(bpy)_3^{3+}$ are summarized in Table I. Simple rate laws, first order in each reactant, were found for these reactions. The detailed kinetic data are reported in Table S-III,[49] Most of the $Co(OH_2)_6^{3+}/Ni^{II}(N_4)$ reactions were found to be pH dependent, with $k_{obsd}(M^{-1}\ s^{-1}) = k_I + k_{II}/(H^+)$. These kinetic data are summarized in Table S-IV.[49] Only the values of k_I are included in Table II,

Reductions of $Ni^{III}(N_4)$ Complexes, Kinetic data for $Ni^{III}(N_4)$ oxidations of $Co^{II}(N_4)$ and $Ru(bpy)_3^{2+}$ complexes are summarized in Table I; kinetic details are presented in Table S-V,[49] Rate constants of these reactions were independent of $[H^+]$ over the range 0.5 M $< [H^+] <$ 1.5 M.

Oxidations of $Cu^{II}(N_4)$ Complexes, The kinetic data for oxidation by $Co(OH_2)_6^{3+}$, $Ru(bpy)_3^{3+}$, and $Fe(phen)_3^{3+}$ are presented in Table I while the details can be found in Table S-III.[49] We were unable to keep any of the $Cu^{III}(N_4)$ complexes for more than a few seconds in aqueous solutions. While the reactions of $Cu^{II}([14]aneN_4)$ with $Co(OH_2)_6^{3+}$, $Ru(bpy)_3^{3+}$, and $Fe(phen)_3^{3+}$ were reasonably straightforward (and pH independent), the oxidations of $Cu^{II}(Me_6[14]4,11\text{-diene}N_4)$ by the polypyridyl complexes were slow and thermodynamically unfavorable so that the results are probably complicated by the rate of product decomposition. Such data have been excluded from Table I.

D, Reactions with Potential Inner-Sphere Oxidants, 1, Reactions with Cl_2^-, The Cl_2^- oxidations of $Ni^{II}(N_4)$ complexes were all very rapid ($\geq 1 \times 10^9\ M^{-1}\ s^{-1}$) and difficult to distinguish rigorously from the decay of scattered excitation light ($\tau_e \sim 60\ \mu s$ for our excitation flash), For example, a rate constant of $9 \times 10^9\ M^{-1}\ s^{-1}$ has been reported for the Cl_2^- oxidation of $Ni^{II}(Me_6[14]4,11\text{-diene}N_4)$[52] (see Table II), For $Ni^{III}(N_4)$ complexes where N_4 = $[14]aneN_4$, $Me_2[14]4,11\text{-diene}N_4$, and $Me_4[14]\text{tetraene}N_4$, generated by this means, the product spectra were stable for nearly 1 ms,

The Cl_2^- oxidations of $Cu^{II}(N_4)$ complexes were relatively slow. The rates of these reactions were generally $[Cl^-]$ dependent with $k_{obsd} = k_4 + k'_4\ (Cl^{-1})$ (Tables II and S-VI[49]); the chloride-dependent pathway is most simply attributed to the reactions of a $\{Cu^{II}(N_4),Cl^-\}$ ion pair. The $Cu^{III}([14]aneN_4)$ and $Cu^{III}(Me_6[14]4,11\text{-diene}N_4)$ products are relatively stable, and the decomposition rate parameters are summarized in Table II (details in Table S-VII[49]), The $Cu^{III}(Me_4[14]\text{tetraene}N_4)$ species was too short lived to be observed in our experiments ($\tau_{1/2} \leq 60\ \mu s$).

2, $Co(OH_2)_5Cl^{2+}$ Oxidations of $M^{II}(N_4)$, Reaction 3 is reported[48] to occur with a rate constant of $1,3 \times 10^6\ M^{-1}\ s^{-1}$ at 22 °C, For this reaction to be competitive with Cl_2^- oxidations of the $Ni^{II}(N_4)$ and some of the $Cu^{II}(N_4)$ complexes requires that $[Co(OH_2)_6^{2+}] \gg [M^{II}(N_4)]$, In most of our experiments $[Co(OH_2)_6^{2+}]$ = 0,1 M while $[M^{II}(N_4)] < 10^{-4}$ M, The product $Co(OH_2)_5Cl^{2+}$ complex equilibrates sufficiently slowly with the medium that it can be regarded as a stable species on the flash photolysis time scale ($\tau_d \sim 0.6$ s for our conditions), The observed reaction rates were generally dependent on $[Cl^-]$, with the observed dependence conveniently expressed

$$k_{obsd} = \frac{k_5 + K_{IP}k'_5[Cl^-]}{1 + K_{IP}[Cl^-]} \qquad (6)$$

When $K_{IP} < 1\ M^{-1}$, this expression reduces to $k_{obsd} \simeq k_5 + K_{IP}k'_5[Cl^-]$ for $[Cl^-] < 0.2$ M. The kinetics data are summarized in Table II, and the details can be found in Table S-VIII.[49]

In the course of this work we have also examined the reaction of $Co(OH_2)_5Cl^{2+}$ with $Fe(OH_2)_6^{2+}$, For this reaction, $k_{obsd} = k_5 + K_{IP}k'_5[Cl^-]$, where we interpret the second term as originating from reactions of the weak chloro–iron(II) complexes such as $Fe(OH_2)_5Cl^+$. We find $k_5 = (1.0 \pm 0.4) \times 10^4\ M^{-1}\ s^{-1}$ and $K_{IP}k'_5 = (5.0 \pm 0.6) \times 10^4\ M^{-2}\ s^{-1}$ (1.0×10^{-5} M $\leq [Fe(II)] \leq 1.2 \times 10^{-4}$ M; 0,5 M $\leq [Cl^-] \leq$ 0.9 M; $[H^+]$ = 1 M in perchlorate/chloride media; 25 ± 1 °C).

3, Oxidations by Macrocyclic Complexes, The $Ni^{III}(N_4)Cl$ complexes formed from Cl_2^- reactions were reasonably tractable species and their behavior as oxidants of $Co^{II}(N_4)$ and $Ni^{II}(N'_4)$ was investigated. Equilibration of the $Ni^{III}([14]aneN_4)Cl$ and $Ni^{III}(Me_4[14]\text{tetraene}N_4)Cl$ complexes with the medium was sufficiently slow that the electron-transfer reactions of these Ni(III) oxidants exhibited simple chloride-independent rate laws. In contrast, the $Ni^{III}(Me_6[14]4,11\text{-diene}N_4)Cl$ complex was

Table III. Rate Constants for $Ni^{III}(N_4)Cl$ Oxidations of $Co^{II}(N'_4)$ and $Ni^{II}(N'_4)$ (25 ± 1 °C; 1 M $HClO_4$)

(N_4) of $Ni^{III}(N_4)Cl$	reductant	k_7, $M^{-1}\ s^{-1}$	$K_f(Ni^{III}(N_4)Cl)$, M^{-1}
$[14]aneN_4$	$Co^{II}(Me_6[14]4,11\text{-}dieneN_4)$	$(3.1 \pm 0.3) \times 10^6$	210 ± 40^a
	$Co^{II}(Me_4[14]tetraeneN_4)$	$(2.1 \pm 0.1) \times 10^7$	
$Me_6[14]4,11\text{-}dieneN_4$	$Co^{II}(Me_6[14]4,11\text{-}dieneN_4)$	$(1.1 \pm 0.5) \times 10^7$	5.1 ± 2.7
	$Co^{II}(Me_4[14]tetraeneN_4)$	$(1.0 \pm 0.4) \times 10^7$	17 ± 7
	$Ni^{II}([14]aneN_4)$	$(4.0 \pm 0.9) \times 10^6$	7.9 ± 2.7
$Me_4[14]tetraeneN_4$	$Co^{II}(Me_6[14]4,11\text{-}dieneN_4)$	$(2.6 \pm 0.2) \times 10^7$	
	$Co^{II}(Me_4[14]tetraeneN_4)$	$(3.4 \pm 0.4) \times 10^7$	
	$Ni^{II}([14]aneN_4)$	$(1.2 \pm 0.1) \times 10^8$	

[a] Reference 54.

Table IV. Summary of Kinetic Data for Reactions of $Cu^{III}(N_4)$ Complexes[a]

oxidant	reductant	$10^{-6}k$, $M^{-1}\ s^{-1}$	$10^{-7}k'$, $M^{-1}\ s^{-1}$
$Cu^{III}([14]aneN_4)$	$Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)_2{}^{2+}$	1.2 ± 0.6	3.0 ± 0.5
	$Co(Me_4[14]tetraeneN_4)(OH_2)_2{}^{2+}$	40 ± 17	63 ± 16
	$Ni([14]aneN_4)^{2+}$	7 ± 1	5.7 ± 0.4
	$Fe(OH_2)_6{}^{2+}$	1.5 ± 0.3	2.6 ± 0.2
$Cu^{III}(Me_6[14]4,11\text{-}dieneN_4)$	$Co(Me_6[14]4,11\text{-}dieneN_4)(OH_2)_2{}^{2+}$	2.7 ± 1.2	
	$Fe(OH_2)_6{}^{2+}$	2.4 ± 1.2	3.6 ± 0.2

[a] 1 M H^+; 25 ± 1 °C; 0.9 M $\geqslant [Cl^-] \geqslant$ 0.1 M (ClO_4^- media); $k_{obsd} = k + k'[Cl^-]$.

Table V. Formal Potentials and Apparent Outer-Sphere Self-Exchange Rate Constants for Some $Ni^{III,II}$ and $Cu^{III,II}$ Couples

equational ligand	$M^{III,II}$	E^f, V^a	$\Delta G^{\ddagger}$,[b] kJ mol^{-1}	k_{exch}, $M^{-1}\ s^{-1}$
$[14]aneN_4$	Ni	1.03^c	44 ± 2 (8)	$4 \times 10^{3 \pm 0.2}$
$Me_6[14]4,11\text{-}dieneN_4$	Ni	1.32^d $(1.26)^e$	65 ± 10 (6)	$10^{0 \pm 2}$
$Me_2[14]4,11\text{-}dieneN_4$	Ni	1.01^f	53 ± 6 (6)	$6 \times 10^{1 \pm 1}$
$Me_4[14]tetraeneN_4$	Ni	1.26^e	~42 (3)	$\sim 3 \times 10^3$
$[14]aneN_4$	Cu	1.25^g	~31 (5)	$10^{6 \pm 1}$ [g]
$Me_6[14]4,11\text{-}dieneN_4$	Cu	1.40^b	~4 (3)	$10^{5 \pm 1}$ [g]
$(H_{-2}Aib_3)^{3-}$	Ni	0.86^h	47^i	550 ± 90^i
$(H_{-3}G_4a)^{3-}$	Ni	0.84^j	37^i	$(1.2 \pm 0.2) \times 10^{5}$ [i]
$(H_{-3}G_3a)^{3-}$	Ni	0.83^j	34^i	$(1.2 \pm 0.2) \times 10^{5}$ [i]
$(H_{-2}Aib_3)^{3-}$	Cu	0.66^k	35.5^l	5.5×10^{4} [l]

[a] vs. NHE. [b] Iterative least-squares fit of data for cross-reactions to eq 8 except for polypeptide complexes at the bottom of the table. Number of different cross-reactions in parentheses. [c] 1.5 M $HClO_4$. [d] Calculated from the forward and reverse rates with $Ru(bpy)_3{}^{3+,2+}$ [e] 6 M $HClO_4$. [f] 1.0 M $HClO_4$. [g] Based on iterative fit of cross-reaction data to the square root form of eq 7. [h] Reference 64a. [i] Murray, C. K.; Margerum, D. W. *Inorg. Chem.* 1983, *22*, 463. Values are based on several cross-reactions and corrected for work terms. [j] References 64c and 64d. [k] Reference 64a. [l] Reference 84a.

sufficiently labile that the electron-transfer reactions of this species were strongly chloride dependent, and described by eq 2, 4, and

$$Cl{-}M(N_4)^{2+} \underset{k_f}{\rightleftharpoons} M^{III}(N_4) + Cl^-$$

$$Cl{-}M(N_4)^{2+} + M'(N'_4)^{2+} \xrightarrow{k_7} M(N_4)^{2+} + Cl{-}M'(N'_4)^{2+} \quad (7)$$

$$k_{obsd} = \frac{k_7 K_f[Cl^-]}{1 + K_f[Cl^-]}$$

Discussion

Evaluation of the kinetic advantage of an inner-sphere electron-transfer pathway requires a reference rate to which the suspected rate advantage may be compared. In the limit that there is no kinetic advantage to the inner-sphere pathway, the rate of outer-sphere electron transfer will tend to dominate the oxidation–reduction chemistry owing to the added complication of metal–ligand dissociation for the inner-sphere pathway. Ideally one would like to reference the free energy independent component of the inner-sphere rate constant to the similar component of the equivalent outer-sphere pathway. This is rarely possible, but it is clear that equivalent outer-sphere pathways must be investigated in order to assess the intrinsic kinetic advantages of various inner-sphere electron-transfer pathways.

A. Outer-Sphere Reactions: Intrinsic Reactivities of the $M^{III,II}(N_4)$ Couples. The $Ni^{III}(N_4)$ and $Cu^{III}(N_4)$ complexes are all very strong oxidants, and they all have smaller Franck–Condon barriers to outer-sphere electron transfer than do the corresponding cobalt complexes. Such factors make systematic study of many of these compounds difficult.

In evaluation of the intrinsic barriers to electron transfer in these systems, we have made the usual corrections for the variations in reactivity with driving force ($\Delta G^{\circ}{}_{ab}$) and for counter-reagent contributions to the intrinsic Franck–Condon barrier ($\Delta G^{\ddagger}{}_{aa}$) by iterative fitting of the cross-reaction kinetic ($\Delta G^{\ddagger}{}_{ab}$) data to the Marcus equation,[3]

$$\Delta G^{\ddagger}{}_{ab} = \frac{1}{2}(\Delta G^{\ddagger}{}_{aa} + \Delta G^{\ddagger}{}_{bb}) + \frac{\Delta G^{\circ}{}_{ab}}{2} + \frac{(\Delta G^{\circ}{}_{ab})^2}{8(\Delta G^{\ddagger}{}_{aa} + \Delta G^{\ddagger}{}_{bb})} \quad (8)$$

For reactions involving the $Ni^{III,II}([14]aneN_4)$ couple, our results are in very good agreement with those of McAuley and coworkers:[56a,61] our data yield $\Delta G^{\ddagger}{}_{bb}(Ni^{III,II})$ = 44 ± 2 kJ mol^{-1} ($k_{exch} \sim 2 \times 10^3\ M^{-1}\ s^{-1}$) compared to McAuley's estimate of $\Delta G^{\ddagger}{}_{bb} \sim 48 \pm 9$ kJ mol^{-1} from cross-reactions and $k_{exch} \sim 10^3\ M^{-1}\ s^{-1}$ from ESR line broadening.[56a]

The cross-reaction data imply that the $Ni^{III,II}([14]aneN_4)$, $Ni^{III,II}(Me_4[14]tetraeneN_4)$, and $Ni^{III,II}(Me_2[14]4,11\text{-}dieneN_4)$ couples all have similar intrinsic barriers to outer-sphere (self-exchange) electron transfer; i.e., $k_{exch} \sim 10^3\ M^{-1}\ s^{-1}$ (Table V). The equatorial ligands of these complexes do not significantly obstruct the axial coordination sites, so that the axial interactions (here presumed to be with water), which are apparently important in the low-spin d^7-Ni(III) complexes,[53] are relatively unimpeded. On the basis of the similarity of the inferred barriers to $Ni^{III,II}$ self-exchange in this group of complexes, one would expect weak

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(60) Moore, J. W.; Pearson, R. G. "Kinetics and Mechanism"; 3rd ed.; John Wiley and Sons: New York, 1981; p 71.

(61) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

Table VI, Estimated Kinetic Advantage of the Cl^--Bridged Inner-Sphere Pathway

oxidant[a]	reductant[a]	no. in Figure 2	k^{OS}, M^{-1} s^{-1}	k^{IS}/k^{OS}	log $(k^{IS}/k^{OS})_{corr}$[b]	no. of electrons in 3-center bond	donor orbital
$Co(OH_2)_6{}^{3+}$(OS) and	$Co^{II}L(2)$	1	10[d]	1.6×10^5 [e,f]	$(\geqslant 5.4)$[f]	3	d_{z^2}
$Co(OH_2)_5Cl^{2+}$(IS)	$Co^{II}L(4)$	2	2.2×10^2 [d]	6.8×10^4 [e,f]	$(\geqslant 4.8)$[f]	3	d_{z^2}
	$Ni^{II}L(1)$	3	86[g]	6.2×10^5	5.3	4	d_{z^2}
	$Ni^{II}L(2)$	4	60[g]	8×10^5	6.2	4	d_{z^2}
	$Ni^{II}L(4)$	5	9×10^2 [g]	1.8×10^2	(3)[h]	4	d_{z^2}
	$Cu^{II}L(1)$	6	2.8×10^3 [g]	2	0.3	4	$d_{x^2-y^2}$
	$Fe(OH_2)_6{}^{2+}$	7	50[i]	200[f]	$(\geqslant 2.7)$[f]	3[j]	d_{xz} or d_{yz}[k]
$Ni^{III}L(1)$	$Co^{II}L(2)$	8	7.6×10^2 [g]	4.1×10^3 [f]	3.6	4	d_{z^2}
	$Co^{II}L(4)$	9	1.3×10^5 [g]	16[f]	1.2	4	d_{z^2}
$Ni^{III}L(2)$	$Co^{II}L(2)$	10	2.8×10^3 [g]	3.9×10^3 [f]	$(\geqslant 3.6)$[f]	4	d_{z^2}
	$Co^{II}L(4)$	11	9.5×10^3 [g]	1.1×10^3 [f]	$(\geqslant 3)$[f]	4	d_{z^2}
	$Ni^{II}L(1)$	12	5.9×10^3 [l]	6.8×10^2	2.2	5	d_{z^2}
$Ni^{III}L(4)$	$Co^{II}L(2)$	13	2.0×10^4 [g]	1.3×10^3 [f]	$(\geqslant 3)$[f,h]	4	d_{z^2}
	$Co^{II}L(4)$	14	5.1×10^5 [g]	67[f]	$(\geqslant 2)$[f,h]	4	d_{z^2}
	$Ni^{II}L(1)$	15	4.7×10^4 [l]	2.6×10^3	(3.4)[h]	5	d_{z^2}

[a] L(1) = [14]aneN_4; L(2) = Me_6[14]4,11-dieneN_4; L(3) = Me_2[14]4,7-dieneN_4; L(4) = Me[14]tetraeneN_4. [b] $(k^{IS}/k^{OS})_{corr}$ obtained by multiplying k^{IS}/k^{OS} by the square root of the ratio of the formation constants of reactant and product chlorocomplexes. [c] Counted as the sum of $d_{z^2} + d_{z^2}' + p_z$ electrons in M(II), M(II)', and Cl, respectively. [d] Reference 10c. [e] Reference 24a. [f] Inner-sphere rate may be limited by substitution on $M(N_4)(OH_2)_2{}^{2+}$ or $Fe(OH_2)_6$. [g] Table I. [h] Formation constant of chloro product is unknown. [i] Reference 70. [j] In a simple one-electron picture. [k] For C_{4v} symmetry d_{xz} and d_{yz} are degenerate. [l] Calculated from E^f values and estimates of k_{exch} with use of eq 8.

but similar axial $Ni^{III}-OH_2$ bonding interactions in each. Coulombic work terms and solvent reorganization should contribute about 17 kJ mol^{-1} to $\Delta G^{\ddagger}{}_{bb}$ in complexes of this size.[9c,10a,d] Most of the remaining ~29 kJ mol^{-1} activation energy can be attributed to the first coordination sphere reorganizational energy ($\Delta G^{\ddagger}{}_{in}$) which must accompany the considerable weakening of the axial ($Ni-OH_2$) interaction on reduction of Ni(III) to Ni(II). That this apparent inner-sphere contribution is about half of that found for the analogous $Co^{III,II}$ couples[10d] is in accord with the expectation that the axial bonding must be weaker for low-spin Ni(III) than for low-spin Co(III).[62,63] The somewhat smaller self-exchange barriers reported[64] for polypeptide–$Ni^{III,II}$ couples (Table VI) are in part a consequence of the smaller Coulombic work term (3–4 kJ mol^{-1}) for the corresponding +1/0 charged couples.

The inferred self-exchange rate of the $Ni^{III,II}(Me_6[14]4,11\text{-diene}N_4)$ couple is appreciably smaller than the self-exchange rates inferred for the other $Ni^{III,II}$ couples (Table V). This is surprising since non-bonded interactions with the equatorial ligand (presumably with the geminal methyl groups) appear to significantly lengthen the weak axial bonds in $Co(Me_6[14]4,11\text{-diene})(OH_2)_2{}^{2+}$,[59] and similar equatorial ligand–axial ligand interactions in the Ni(III) and Ni(II) complexes, in combination with the reasoning outlined above, would predict a smaller value of $\Delta G^{\ddagger}{}_{in}$ (or of $\Delta G^{\ddagger}{}_{bb}$) for this complex. The reversed ordering of observed reactivities implicates some equatorial ligand rearrangement in the $Ni^{III,II}(Me_6[14]4,11\text{-diene}N_4)$ couple. In support of this inference, it is to be noted that the equatorial ligand–N–Ni^{II} bond lengths tend to be several picometers shorter than the corresponding Co^{III}–N (or Co^{II}–N) bond lengths in these complexes,[10d,59,63] and that some of the macrocyclic ligands of $Ni^{II}-(N_4)$ complexes are "buckled" to such an extent that geminal methyl groups very nearly occupy axial coordination positions.[63] These same ligands have been found to have strong Ni^{III}-axial bonds.[53]

The $Cu^{III}(N_4)$ complexes have proved to be powerful and reactive oxidants, and generally have very short lifetimes. We have been able to obtain reasonably good cyclic voltammometric data for the $Cu^{III,II}(Me_6[14]4,11\text{-diene}N_4)$ couple in aqueous media. Electrochemical oxidations of the other couples were either irreversible (presumably owing to rapid product decomposition) or occurred at potentials too positive for good electrode response in our media. Electrochemical data exist for several of these couples in nonaqueous media;[55b,65] however, differences in junction potentials and solvation prevent these observations from being a reliable basis for the estimation of potentials for $Cu^{III,II}(N_4)$ couples in aqueous media.

We have been able to study some $Cu^{III}(N_4)$ reactions by generating the oxidant flash photolytically as described above. While these reactions were always carried out in chloride media, their rates were only weakly dependent on $[Cl^-]$, and we attribute the chloride-independent components of such reactions to outer-sphere electron-transfer reactions. By this means we have been able to obtain rate constants for some $Cu^{III}(N_4)$ oxidations of $Co(N_4)(OH_2)_2{}^{2+}$ and $Fe(OH_2)_6{}^{2+}$. For a combination of reasons (including oxidant stability, small $Cu^{II}(N_4)$ absorptivity, rapid reaction with Cl_2^-, lack of complicating photochemistry, etc.) reactions of $Cu^{III}([14]aneN_4)$ have proved to be the most convenient to investigate. By an iterative fitting of the rate constants and equilibrium constants of the cross-reactions (Table I) we have found that a potential of ~1.25 V and a self-exchange rate constant of $10^{6\pm1}$ M^{-1} s^{-1} give the best fit to the kinetic data. This may be compared to $E_{1/2}$ = 1.35 V (vs. SCE) for the $Cu^{III,II}([14]aneN_4)$ couple obtained in acetonitrile by Fabbrizzi and co-workers,[65] E^f = 1.40 V for the aqueous $Cu^{III,II}(Me_6[14]4,11\text{-diene}N_4)$ couple, and the expectation of more positive potentials for $M^{III,II}(Me_6[14]4,11\text{-diene}N_4)$ than for $M^{III,II}([14]aneN_4)$ couples.[33,65]

The small intrinsic reorganizational energy inferred for the $Cu^{III,II}(N_4)$ couples probably originates from the change in equatorial Cu–N bond lengths[66] with very little contribution arising from the undoubtedly very weak axial interactions; however, differences in axial interactions and equatorial ligand strain un-

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[62] One expects the $Ni^{III}-OH_2$ bond length to be intermediate between those of the axial bonds in the corresponding $Co^{III}(N_4)(OH_2)_2$ and $Co^{II}(N_4)(OH_2)_2$ complexes.[10d,33,53,59,63] While the actual difference between $M^{III}-OH_2$ and $M^{II}-OH_2$ bond lengths could well be greater for the nickel than for the cobalt complexes, the substantial decreases in effective $M-OH_2$ force constant associated with their longer axial bonds should adequately account for the smaller values of $\Delta G^{\ddagger}{}_{in}$ found for the $Ni^{III,II}$ couples (note that the force constant ratio, $\sim f_{II}f_{III}/(f_{II} + f_{III})$, contributing to $\Delta G^{\ddagger}{}_{i}$ is very sensitive to f_{II} and approaches f_{II} when $f_{III} \gg f_{II}$).

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doubtedly make some contributions to $\Delta G^{\ddagger}_{in}$.

Overall, we find the intrinsic barriers to outer-sphere electron transfer to be far greater in low-spin $Co^{III,II}(N_4)$ couples than in the analogous $Ni^{III,II}(N_4)$ couples. The limited evidence now at hand indicates greater variability and slightly larger intrinsic barriers for the low-spin $Ni^{III,II}(N_4)$ than for the $Cu^{III,II}(N_4)$ couples. These activation barriers, and the resulting reactivity patterns, are most likely dominated by Franck–Condon factors. Although we do not yet have precise knowledge of the structural parameters contributing to the Franck–Condon factors for the nickel and copper complexes, there is little doubt that these contributions must be smaller than those for the $Co^{III,II}(N_4)$ complexes. The details of donor–acceptor orbital occupation are not distinguishable as factors contributing to outer-sphere electron-transfer reactivity patterns among these Ni and Cu complexes.[66]

B. **Phenomenology of Coupled Cl^- and Electron-Transfer Processes.** Because the transition-state geometry is relatively well defined by a three-center-bridging interaction, there is considerable potential for large contributions of donor–acceptor orbital symmetry effects to inner-sphere electron-transfer reactions. Indeed, such contributions have often been postulated.[17,18-22,67] The major focus of this work has been the examination of reaction pathways in very closely related series of macrocyclic complexes for manifestations of the effects of variations in donor–acceptor orbital occupations. We have chosen reactions with a potential for mediation by a Cl^--bridging ligand, because chloride-bridged pathways have been found to exhibit a 10^6–10^7-fold intrinsic rate enhancement over outer-sphere pathways in both self-exchange reactions ($Co(N_4)(OH_2)Cl^{2+}/Co(N_4)(OH_2)_2^{2+}$) and cross-reactions of $Co(N_4)(OH_2)_2^{2+}$,[24a] and because there are relatively few complicating features (or side reactions) in chloride media.

The reactions of $Co(OH_2)_5Cl^{2+}$ have proved particularly useful. One would expect this species to be a poorer oxidant than $Co(OH_2)_6^{3+}$ by 0.1 to 0.2 V.[68] The tendency of the weaker oxidant to be less reactive (in outer-sphere electron-transfer reactions) will be at least partly compensated by the smaller charge and possibly by smaller first coordination sphere reorganizational energies.[69,70] In any event, the smallest ratio of rate constants for $Co(OH_2)_5Cl^{2+}/M^{II}$ to $Co(OH_2)_6^{3+}/M^{II}$ reactions is about 2, found for $M^{II} = Cu^{II}([14]aneN_4)$. This is clearly an upper limit for the ratio of *outer-sphere* reaction rates of $Co(OH_2)_5Cl^{2+}$ and $Co(OH_2)_6^{3+}$. As a matter of convenience in the discussion below, we have used the rates of $Co(OH_2)_6^{3+}$ reactions as the reference reactions for the inner-sphere rate advantage of $Co(OH_2)_5Cl^{2+}$.

Since substitution at a labile metal center is a prerequisite for the inner-sphere pathway[2,16,17] this pathway can only be advantageous, compared to the outer-sphere pathway, if at least one of the following conditions obtains: (a) there is a distinct thermodynamic advantage to the inner-sphere pathway; or (b) the activation barrier for the inner-sphere pathway is much smaller than that for the equivalent outer-sphere pathway. The first condition appears to be dominant when $-CH_3$ functions as a "bridging" group,[10a,24c] but appears to be of much less consequence for halide-bridging groups. The issues we wish to explore are the origin of the purely kinetic advantage, if any, of the Cl^--bridged inner-sphere pathway. To this end the ratio of second-order rate constants for the inner-sphere and outer-sphere processes, k^{IS}/k^{OS}, should be an approximate indication of the inner-sphere kinetic advantage provided the contributions of ΔG° are the same for both pathways. In general, this will not be the case, and the ratio k^{IS}/k^{OS} should be extrapolated to similar ΔG° contributions in the rate constants. It is convenient to represent this limiting ratio as

$$(k^{IS}/k^{OS})_{\Delta G^\circ \to 0} = \chi$$

The effect of variations of ΔG° on the rates of inner-sphere reactions are not well established, but there are some hints[2,24a,25-32] that the dependence may not be much different from that for outer-sphere reactions, i.e., as in eq 8. Furthermore, we have previously noted[20a] that k^{IS}/k^{OS} is comparably large whether one compares $Co(N_4)(OH_2)Cl^{2+}/Co(N_4)(OH_2)_2^{2+}$ (k^{IS}) and $Co(N_4)(OH_2)_2^{3+}/Co(N_4)(OH_2)_2^{2+}$ (k^{OS}) self-exchange reactions ($\Delta G^\circ = 0$) or cross-reactions of the $Co(N_4)(OH_2)_2^{2+}$ species ($\Delta G^\circ < 0$ for both inner-sphere and outer sphere reactions) at similar values of ΔG°. The comparisons we are making, of the order-of-magnitude variations in k^{IS}/k^{OS}, are largely isoergonic in the two pathways.

Our approach is usefully illustrated in the $Co(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ reaction, for which $k^{IS} = 1.0 \times 10^4\ M^{-1}\ s^{-1}$.[71] For the $Co(OH_2)_6^{3+}/Fe(OH_2)_6^{2+}$ reaction, $k^{OS} = 50\ M^{-1}\ s^{-1}$,[72] so $k^{IS}/k^{OS} = 2 \times 10^2$. This is indicative of a considerable kinetic advantage for the inner-sphere pathway, but the rate ratio is not quite isoergonic since there is a difference in stability of the $M(OH_2)_5Cl^{2+}$ complexes.[73-75] We assume that this small driving force correction affects the rate constants as $(K_f(CoCl^{2+})/K_f(FeCl^{2+}))^{1/2}$ as implied by eq 8, so $(k^{IS}/k^{OS})_{corr} \simeq 5 \times 10^2$. Since the rate of water exchange on $Fe(OH_2)_6^{2+}$ is only $k_2 = 3 \times 10^6\ s^{-1}$,[76] and the limiting rate for substitution of a dipositive ligand could be $10^5\ M^{-1}\ s^{-1}$ (assuming for substitution, $k_{obsd} = K_o k_w$; K_o is the outer-sphere association, or ion pair, constant), the $Co(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ reaction may approach the limit for substitution of water on iron(II). For comparison, the $Co(OH_2)_5Cl^{2+}$ oxidations of $Co(N_4)(OH_2)_2^{2+}$ appear to be substitution limited (since they occur in a range where the rate becomes independent of ΔG°)[24a] when $k_{IS} \sim 10^7\ M^{-1}\ s^{-1}$ and $k_w \sim 10^8$–$10^9\ s^{-1}$.[59] Thus, the observed rate constants yield a ratio, $(k^{IS}/k^{OS})_{corr}$, which may be smaller than the intrinsic rate advantage (χ) of the inner-sphere pathway.

If one compares the value of k^{IS}/k^{OS} obtained above, for the $Co(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ reaction, to $k^{IS}/k^{OS} \sim 5$ reported for the $Fe(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ self-exchange reactions,[77-81] it appears that the Cl^--bridged pathway is more than two orders of magnitude more important for the Co–Fe cross-reaction than for the $Fe^{III,II}$ self-exchange. This apparent kinetic advantage of the Cl^--bridged pathway could be largely a reflection of the very large intrinsic kinetic advantage of the Cl^--bridged pathway in $Co^{III,II}$ couples ($\sim 10^6$ for $Co(N_4)$ couples)[24a] if the contributing components can be approximately factored: $\chi(Co,Fe) \sim (\chi$-

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(66) This argument is based on expected differences in Cu^{III}-N ($\sim$190 pm) and Cu^{II}-N ($\sim$200 pm) bond lengths; details may be found in ref 10a, p 154. We would estimate $\Delta G^{\ddagger}_{in} \sim$ kJ mol^{-1} and $\Delta G^{\ddagger}_{out} + w \simeq 17$ kJ mol^{-1} for these systems.

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(69) Note that the $Co(N_4)Cl_2^+/Ru(NH_3)_6^{2+}$ reactions[10d,70a] tend to be 10–100 times faster than the corresponding $Co(N_4)(OH_2)_2^{3+}/Ru(NH_3)_6^{2+}$ reactions[10d,70b] even though the latter appear to have larger equilibrium constants.

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(79) The actual value of k^{IS}/k^{OS} for $Fe(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ may be greater than implied in ref 74 since most outer-sphere cross-reaction data suggest $k^{OS} \gg 5\ M^{-1}\ s^{-1}$.[80] It has been suggested[80] that the $Fe(OH_2)_6^{3+}/Fe(OH_2)_6^{2+}$ reaction is mediated by water bridging. On the basis of these considerations, a plausible estimate of k^{IS}/k^{OS} for $Fe(OH_2)_5Cl^{2+}/Fe(OH_2)_5^{2+}$ would be $\sim 10^3$.

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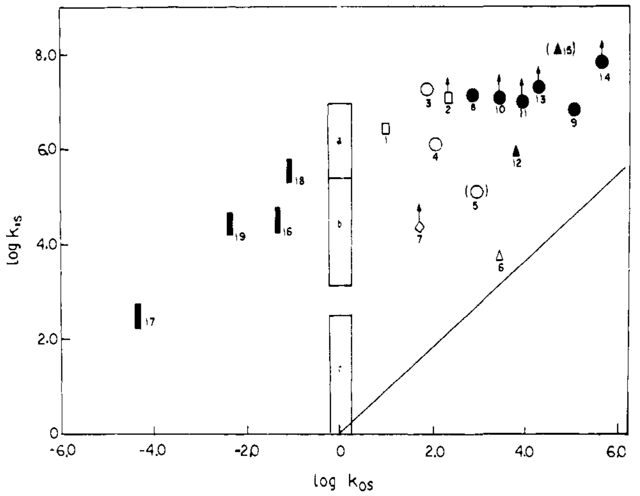

Figure 2. Graphical representation of the inner-sphere rate advantage for chloride-mediated reactions of several complexes. Open points (1–6) are based on the reaction rates with $Co(OH_2)_5Cl^{2+}$ (k^{IS}) and $Co(OH_2)_6^{3+}$ (k^{OS}), squares for $Co^{II}(N_4)$, circles for $Ni(N_4)$, triangle for $Cu^{II}(N_4)$ substrates, and diamond for Fe^{II}. For key to numbers 1-15 refer to Table VI. Closed circles are for $Ni^{III}(N_4)Cl/Co^{II}(N'_4)$, and closed triangles are for $Ni^{III}(N_4)$ reactions. Closed rectangles are based on $Co^{III}(N_4)(OH_2)Cl/Co^{II}(N_4)$ (k^{IS}) and $Co^{III}(N_4)(OH_2)_2/Co^{II}(N_4)$ (k^{OS}) self-exchange rates (data from refs 10d, 24a,b, and C.-L. Wong, unpublished work). Lower limits are indicated by vertical arrows for those inner-sphere rates that are likely to be limited by substitutions on $Co^{II}(N_4)(OH_2)_2$. Parentheses indicate that we were unable to correct for differences in reactant and product M^{III}–Cl formation constants. Macrocyclic ligands in self-exchange reactions are as follows: $Me_4[14]$tetraeneN$_4$ (16); $Me_6[14]4,11$-dieneN$_4$ (17); Me_2pyo[14]trieneN$_4$ (18); and $Me_2[14]4,7$-dieneN$_4$ (19). Boxes in the center of the figure indicate the ranges of the inner-sphere rate advantage (χ) for different classes of compounds extrapolated to $k^{OS} = 1$: (a) Co^{III}–Co^{II} and Co^{III}–Ni^{II} reactions; (b) Ni^{III}–Co^{II} reactions; (c) Ni^{III}–Ni^{II} and Co^{III}–Cu^{II} reactions.

$(Co,Co)\cdot\chi(Fe,Fe))^{1/2}$. At face value these observations suggest a reactivity order $\chi(Co,Co) > \chi(Fe,Fe)$. Similar orderings of reactivity patterns have led to the postulated correlation of the significance of the inner-sphere pathway to the symmetry of donor and acceptor orbitals.[67,82]

In comparing the $Co(OH_2)_6^{3+}$ and $Co(OH_2)_5Cl^{2+}$ reactions with $M^{II}(N_4)$ and $Fe(OH_2)_6^{2+}$ complexes (Tables I, II, and VI), it is to be noted that the most effective reductant toward $Co(OH_2)_6^{3+}$ is the poorest reductant of $Co(OH_2)_5Cl^{2+}$: $Cu^{II}([14]aneN_4)$. It is also pertinent that the reaction of $Co(OH_2)_6^{3+}$ with $Cu^{II}([14]aneN_4)$ is an exception among the $M^{II}(N_4)$ reactions studied, in its independence of pH (in the range of $2 \leq pH \leq 1$).[83] As noted above, a small first coordination sphere reorganizational barrier for the low-spin $Cu^{III,II}(N_4)$ couples is reasonable and appears to be generally observed. That $Cu^{II}([14]aneN_4)$ does not significantly discriminate between the $Co(OH_2)_6^{3+}$ and $Co(OH_2)_5Cl^{2+}$ oxidants provides no evidence for the reaction pathway for the later oxidant, but it does demonstrate that the inner-sphere pathway offers no significant rate advantage for the $Cu^{III,II}(N_4)$ couple. The contrast in kinetic behavior is dramatic for the same oxidants with $Co^{II}(N_4)$, $Ni^{II}(N_4)$, and even $Fe(OH_2)_6^{2+}$. The observed order of magnitude variations in the selective reactivity toward $Co(OH_2)_5Cl^{2+}$ (i.e., in k^{IS}/k^{OS}) are strong evidence for a kinetically important inner-sphere pathway in all these systems. That values of k^{IS}/k^{OS} based on the $Co(OH_2)_5Cl^{2+}$–$Co(OH_2)_6^{3+}$ comparison with $Co^{II}(N_4)$ substrates approach those obtained from $Co^{III,II}(N_4)$ self-exchange reactions,[24a] despite the limitations of rate imposed by Co^{II}–OH_2 bond breaking and the order of magnitude difference in the individual rate constants, is in accord with the mechanistic inference and argues that such large values of k^{IS}/k^{OS} (10^5–10^7) are a characteristic of the Co–Cl–Co transition state for the Cl^--bridged reactions (see Figure 2).

The $Co(OH_2)_5Cl^{2+}/Ni^{I}I(N_4)$ reactions are roughly comparable in rate to the $Co(OH_2)_5Cl^{2+}/Co^{II}(N_4)$ reactions, but inner-sphere pathways of low-spin d^8 Ni(II) are not likely to be rate limited by axial substitution.[57] Considerations outlined above indicate that these reactions are 10^4–10^5 times faster than expected for the equivalent outer-sphere electron-transfer processes; i.e., $k^{IS}/k^{OS} \sim 10^{4\pm1}$ for $Co^{III}/Ni^{II}(N_4)$. The intrinsic advantage of the inner-sphere pathway is very large with $Ni^{II}(N_4)$ and $Co^{II}(N_4)$ substrates. Note that on the time scale of our flash photolysis studies, the $Ni^{III}(N_4)$ product of the $Co(OH_2)_5Cl^{2+}$ reactions was always $Ni^{III}(N_4)Cl$. For N_4 = [14]aneN$_4$, $Me_2[14]4,7$-dieneN$_4$, and $Me_4[14]$tetraeneN$_4$ this product could be generated in nonequilibrium amounts, since anation and aquation are relatively slow in these Ni(III) complexes. This and the relative rate considerations noted indicate that these are indeed inner-sphere reactions.

The stability of $Ni^{III}(N_4)Cl$ makes it relatively easy to use as an oxidant. We have used $Ni^{III}([14]aneN_4)Cl$, $Ni^{III}(Me_4[14]$tetraeneN$_4)Cl$, and $Ni^{III}(Me_6[14]$-4,11-dieneN$_4)Cl$ (this last species was, of course, always in equilibrium with the solution) as oxidants toward $Co^{II}(N_4)$ and $Ni^{II}(N_4)$ complexes. Many of these reactions are again limited by the rate of water loss on Co(II), but those for which such restrictions are not likely to be a problem (see Table VI) indicate that $(k^{IS}/k^{OS})_{corr} \sim 10^3$–$10^4$ for such combinations. This approaches the range of observations in $Co(OH_2)_5Cl^{2+}/Ni^{II}(N_4)$ reactions (see Figure 2) and suggests that the intrinsic inner-sphere rate advantage for Ni–Cl–Co transition states does not depend on the details of formulating the inner-sphere transition states; i.e., it is independent of which metal is the oxidant, independent of the nominal coordination numbers of the reactants, etc.

C. Likely Origins of the Inner-Sphere Rate Advantage in the Cl^--Bridged Systems. The intrinsic kinetic advantage for the inner-sphere, Cl^--bridged pathway shows a distinct dependence on the metal: $\chi(Co,Co) \geq \chi(Co,Ni) > \chi(Ni,Ni) > \chi(Co,Cu)$ (see Figure 2). This is in part in the order of the increasing number of electrons in the formal transition state M–Cl–M′ three-center bond; counting the occupation of the d_{z^2} orbitals of the homolytically dissociated divalent metals, and the p_z orbital of the Cl radical, these are respectively 3, 4, 5, and 4. Since a three-center-bonding arrangement is associated with one bonding, one non-bonding, and one anti-bonding orbital, the order of decrease in $\chi(M,M')$ can be associated with an increase in the number of electrons in this orbital system. The greatest number of electrons along the z axis (5 for Ni/Ni) would have to populate the antibonding orbital, and thus de-stabilize the transition-state-bridging interaction. The three- and four-electron cases exhibit very considerable rate advantages for the inner-sphere pathway. That $\chi(Co,Ni) \sim \chi(Ni,Co)$ argues against any simple dependence on reactant substitutional properties.

The Co/Ni reactions raise some interesting conceptual points. Our description of the transition state is referenced to the homolytic dissociation limit (Co^{II}, $\cdot X$, Ni^{II}). Referenced to this limit, the formal description of a three-center transition-state-bonding interaction is independent of the precise electron configurations of the reactants, i.e., whether the reactants are Co^{III} and Ni^{II} (d^6/d^8) or Ni^{III} and Co^{II} (d^7/d^7). Both reactant electron configurations result in four electrons in the M–X–M′ transition-state bond.

The failure to observe a significant rate enhancement in $Co(OH_2)_5Cl^{2+}/Cu^{II}(N_4)$ reactions is very interesting. Owing to the steric constraints of the macrocyclic ligand, the formal bonding interactions are the same for (Co–Cl–Ni) and (Co–Cl–Cu) transition states (three-center, four-electron bond). However, $\chi(Co,Cu)$ is much less than $\chi(Co,Ni)$ and probably smaller in magnitude than $\chi(Ni,Ni)$. On the other hand, this is the single system investigated in which the electron transfer–donor orbital ($d_{x^2-y^2}$ on Cu^{II}) is sterically constrained to be orthogonal to the

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[82] Stritar, J. A.; Taube, H. *Inorg. Chem.* **1969**, *8*, 2281.

[83] In view of the strongly oxidizing couples involved, one might be tempted to postulate a water bridged pathway[10c] (as suggested by a referee) for the $Co(OH_2)_6^{3+}/Cu^{II}(N_4)$ reactions. The insensitivity to variations in pH and the correlations with other outer-sphere reaction rates of the $Co(OH_2)_6^{3+,2+}$ and $Cu^{III,II}(N_4)$ couples support the proposed outer-sphere pathway.

axis of the (M–X–M) transition-state bond, We propose that this orthogonality results in an unfavorable inner-sphere pathway in Co^{III}/Cu^{II} reactions, It is to be noted that this prohibition must be quite strong in view of the preference of $Co^{III,II}$ couples for a chloride-bridged, electron-transfer pathway.

The instability of $Cu^{III}(N_4)$ complexes has frustrated our attempts to examine further the validity of the proposed relationship between electron-transfer-oribtal/transition-state-bonding-orbital orthogonality and the kinetic advantage of inner-sphere electron-transfer pathways. For example, attemps at the reactions of Cu^{III}(2,4-O_2[14]anato(−2)N_4) with $Co^{II}(N_4)$ complexes, even at a compromise pH of 3, were complicated by the apparent decomposition of the Cu^{III} complex leading to poorly reproducible rates; our limited observations indicate that $1 \leq \chi(\mathrm{Cu,Co}) \leq 4 \times 10^2$ for these reactions. More significant are the surprisingly slow $Cl_2^-/Cu^{II}(N_4)$ reactions (Table II). The Cl_2^- radical is a powerful oxidant ($E^f \simeq 2.6$ V) with a strong tendency to react by "oxidative addition" rather than by simple outer-sphere electron transfer, The results argue that the $Cu^{II}(N_4)$ substrates are somewhat more reluctant to react by such a pathway than are $Co^{II}(N_4)$ and $Ni^{II}(N_4)$ complexes.

It is important to note that while the reactions

$$Cl_2^- + M^{II}(N_4) \rightarrow Cl^- + M^{III}(N_4)Cl$$

are formally comparable to the coupled ligand–electron transfer reactions

$$M^{III}\text{–}Cl + M^{II}(N_4) \rightarrow M^{II} + MI^{II}(N_4)Cl$$

of concern in this study, reactions that form metastable adducts as product species may not be conveniently described in terms of a homolytic reaction coordinate. Reactions in which metastable adducts form are likely to involve relatively strong M–X–M′ transition-state-bonding interactions (or relatively small changes in M–X bond lengths), and few features of the approach we have considered are likely to apply. Common examples that appear to involve M–X–M′ transition-state interactions but not necessarily M–X homolysis are reactions involving the $IrCl_6^{2-,3-}$ and $Fe(CN)_6^{3-,4-}$ couples, Margerum and co-workers[64,84] have combined such reactants with polypeptide–$Cu^{III,II}$ couples and obtained results that they interpret in terms of a dominant inner-sphere pathway. Unfortunately, interpretation of the original report[84a] was complicated by a failure to take into account a large work term correction (arising from the difference in charge types of the cross-reaction and the component self-exchange reactions) in the estimates of the rate constant for outer-sphere electron transfer. Making an approximate work term correction, one finds (k_{obsd}/k^{OS}(calcd)) < 10^2 for all the reactions reported[64,84] and (k_{obsd}/k^{OS}(calcd)) ~ 1 for several of the reactions. These small ratios of observed to calculated rate constants are not particularly helpful in establishing the reaction mechanism, but they do suggest that "k^{IS}/k^{OS}" is small for such reactions. In the present context it may be more significant that the polypeptide–$Cu^{III,II}$ cross-reactions (and self-exchange reactions) were found to be independent of [Cl^-].[84a]

In a systematic discussion of the reaction coordinate, the "forbiddenness" of the $Co(OH_2)_5Cl^{2+}/Cu^{II}(N_4)$ reaction should be treated in terms of a forbidden crossing from the reactant and/or product potential energy surfaces to the three-center transition state. This is most conveniently discussed in terms of a hypothetical $Cu^{III}(N_4)Cl/Cu^{II}(N_4)$ self-exchange reaction. The homolytic cleavage of the $Cu^{III}(N_4)(Cl^-)$ "bond", to yield the $Cu^{II}(N_4)$ product, does not correlate with the ground-state $Cu^{II}(N_4)$ product since the Cu $d_{x^2-y^2}$ orbital cannot contribute to the Cu–Cl "bonding" interaction along the z axis. Rather, any such interaction must involve high-energy Cu orbitals (e.g., 4s or 4sp) and be correlated with a high-energy Cu^{II} excited state.

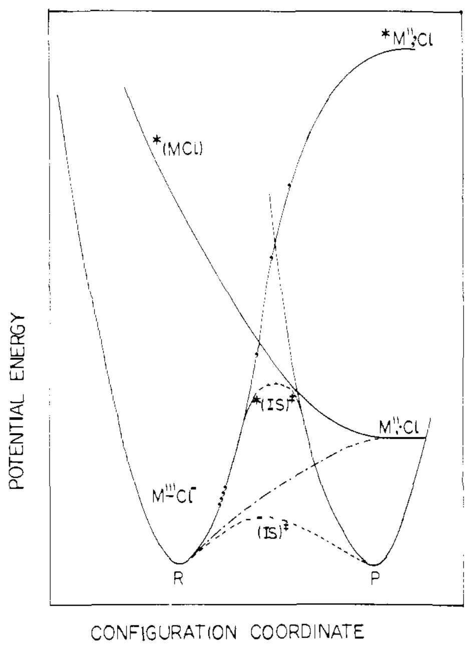

Figure 3, Qualitative correlation diagram representing the effects of a forbidden crossing on the transition-state energetics for an inner-sphere reaction. Solid curves represent (lower curve) homolytic dissociation of the (M^{III}–Cl^-) ground state to an electronically excited metallo fragment ($*M^{II}$,·Cl) and (upper curve) an unbound charge-transfer state correlating with the ground-state M^{II} electronic configuration ($*(MCl)_{CT} \rightarrow M^{II}$,·Cl). The dashed curve indicates the effect of the forbidden crossing on the hypothetical transition state for the inner-sphere pathway ($*(IS)^‡$). If the $M^{III}Cl^-$ ground-state homolysis correlated smoothly with product ground states (M^{II}, Cl) as in the dotted curve, this would result in a lower-energy inner-sphere transition state $(IS)^‡$. Approximate energy relations are based on charge-transfer and thermal energetics in a ($Cu^{III}(N_4)$,Cl^-)–$Cu^{II}(N_4)$ system. Reactant (R) and product (P) potential energy surfaces are included for convenience in correlating with transition states, but product excited states, dissociation limits, etc., are omitted for clarity.

The resulting promotion energy is consistent with a weak $Cu^{III}(N_4)$–Cl^- bond. The approximate correlation diagram is presented in Figure 3, Assuming overall D_{4h} transition-state symmetry, the transition-state-bonding interaction would have A_{2u} symmetry, and crossing to this configuration from the $Cu^{III}(N_4)Cl/Cu^{II}(N_4)$ potential energy surface for the reactants in their ground states is forbidden owing to the B_{1g} (ground state) symmetry of $Cu^{II}(N_4)$, In lower symmetry (e.g., C_{4v}) the crossing from the ground-state surface would still be symmetry forbidden ($B_1 \rightarrow A_1$), and considerable promotion energy (3d → 4s) would be required to achieve the lowest excited state for which crossing to the transition state is allowed. The forbidden crossing to the transition state and mixing of the excited states results in a large value of $\Delta G^‡_{IS}$ as illustrated in Figure 3.

Some similarities of the $Cu^{III,II}$ and $Fe^{III,II}$ couples might be expected, Again, one has a forbidden crossing from the ground-state potential energy surface to the transition state (E → A); however, the promotion energy to the correlated excited states, some mixture of ($^5E;t^3e^3$)Fe(II) and ($^4T_1;t^4e$)Fe(III), should be smaller for the iron couple. This smaller promotion energy could account for a meaningful three-center transition-state-bonding interaction and the observation of a small value of k^{IS}/k^{OS} for the $Fe(OH_2)_5Cl^{2+}/Fe(OH_2)_6^{2+}$ couple.[77-81] A cobalt partner in the transition-state three-center bond should lead to a stronger interaction and larger value of k^{IS}/k^{OS}, as observed. As a final comment on the iron system, we note that for a C_{2v} transition-state symmetry, the ground-state/transition-state surface crossing is symmetry allowed. This may account for the apparent effectiveness of hydroxide bridging in promoting the $Fe(OH_2)_6^{3+,2+}$ self-exchange.[81]

The analogous descriptions of Co/Ni or Ni/Ni reactions do not involve symmetry-forbidden ground-state/transition-state surface crossings, nor do they require correlation with excited

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[84] (a) Koval, C. A.; Margerum, D. W. *Inorg. Chem.* **1981**, *20*, 2311. (b) Rybka, J. S.; Margerum, D. W. *Ibid.* **1981**, *20*, 1453. (c) Anast, J. M.; Margerum, D. W. *Ibid.* **1982**, *21*, 3494.

[85] The axial interaction energy need not exceed that associated with normal solvation interactions. Real but very weak, axial Cu-ligand interactions are routinely found for $Cu^{II}(N_4)$ complexes.

electronic states of the reactants,

D, Summary and Conclusions, By using macrocyclic ligand complexes it has been possible to systematically examine the response of simple electron-transfer reactivity patterns to changes in reactant electron configuration. As one would anticipate there is no special effect, over and above variations in Franck–Condon factors, detectable for reactions approaching the outer-sphere limit. In contrast, a large variation in reactivity patterns is observed for inner-sphere, Cl^--bridged, electron-transfer reactions. In order to evaluate the effectiveness of the inner-sphere pathway in promoting electron transfer we have approximated the free energy independent reactivity, or the intrinsic rate advantage of the inner-sphere pathway (χ) in terms of the ratio of the rate constants for inner-sphere and outer-sphere electron transfer, k^{IS}/k^{OS}. For $Co(OH_2)_5Cl^{2+}$ oxidations (k^{OS} determined from the corresponding $Co(OH_2)_6{}^{3+}$ reactions) of $M^{II}(N_4)$ complexes, $\chi = 10^4$–10^6, 10^5–10^6, and 2, for M = Co, Ni, and Cu, respectively. For $M^{III}(N_4)Cl/M^{II}(N'_4)$ reactions $\chi = 10^{6\pm1}$ and $10^{1\pm2}$, respectively, for M = Co and Ni. Finally, for the $Co(OH_2)_5Cl^{2+}/Fe(OH_2)_6{}^{2+}$ reactions $\chi \geq 10^3$ compared to $\chi \sim 10$ reported for the $Fe(OH_2)_5Cl^{2+}/Fe(OH_2)_6{}^{2+}$ reaction,

The results of this work suggest the following general features for reactions in which electron transfer is coupled with transfer of a bridging ligand;

1. A homolytic (M^{III}–X^-) bond-dissociation coordinate is a useful starting place for discussion of the inner-sphere reaction coordinate,

2. With reference to this coordinate, the transition state for inner-sphere electron transfer may be usefully described in terms of a three-center, M–X–M bond formalism, constructed from metal d_{z^2} and X p_z orbitals (for $\sigma^* \rightarrow \sigma^*$ reactions).

3. The stability of the inner-sphere transition state tends to decrease with increases in the number of electrons in a three-center transition-state bond. In particular, three-electron and four-electron transition-state-bonding configurations result in an appreciable kinetic advantage for the inner-sphere pathway while there is relatively little advantage to the five-electron configuration.

4. The inner-sphere pathway is kinetically advantageous only if the three-center-bonding interaction also mixes the electron-transfer donor and acceptor orbitals. This amounts to a symmetry requirement and is best formulated in terms of the electronic configurations of the individual metal reactants that correlate with the electronic configuration of the three-center (nM–X–M′) bond. The symmetry constraints can then be discussed in terms of symmetry-allowed or -forbidden crossing from the reactant potential energy surface to the three-center transition state.

This approach provides a model for the transition state in reactions in which transfer of a bridging ligand occurs in concert with electron transfer. The transition-state model is referenced to the homolytic dissociation limit and thus does not include a detailed description of the association of reactant species to form the bridged transition state; more specifically, the larger reactivity variations are attributed to properties of the three-center transition state rather than to peculiarities of precursor complexes. The data available regarding free energy independent inner-sphere reactivities are in reasonable accord with the view that the electronic properties of the three-center transition-state M–X–M′ bond are of much greater importance to reactivity variations than are the substitutional properties of the reactant complexes.

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Registry No, $Ni^{II}([14]aneN_4)$, 46365-93-9; $Ni^{III}([14]aneN_4)$, 66199-97-1; $Ni^{III}([14]aneN_4)Cl$, 66199-96-0; $Cu^{II}([14]aneN_4)$, 52304-87-7; $Cu^{III}([14]aneN_4)$, 87533-28-6; $Co^{II}([14]aneN_4)$, 61872-12-6; $Ni^{II}(Me_6[14]4,11\text{-diene}N_4)$, 18444-38-7; $Ni^{III}(Me_6[14]4,11\text{-diene}N_4)$, 66139-82-0; $Ni^{III}(Me_6[14]4,11\text{-diene}N_4)Cl$, 82871-90-7; $Cu^{II}(Me_6[14]4,11\text{-diene}N_4)$ (racemic), 48186-22-7; $Cu^{II}(Me_6[14]4,11\text{-diene}N_4)$ (MeSO), 48186-23-8; $Cu^{III}(Me_6[14]4,11\text{-diene}N_4)$, 87533-29-7; $Co^{II}(Me_6[14]4,11\text{-diene}N_4)$, 33247-96-0; $Co^{III}(Me_6[14]4,11\text{-diene}N_4)(H_2O)_2$, 17815-30-4; $Ni^{II}(Me_4[14]\text{tetraene}N_4)$, 53277-04-6; $Ni^{III}(Me_4[14]\text{tetraene}N_4)$, 87533-25-3; $Ni^{III}(Me_4[14]\text{tetraene}N_4)Cl$, 87533-27-5; $Cu^{II}(Me_4[14]\text{tetraene}N_4)$, 71170-97-3; $Co^{II}(Me_4[14]\text{tetraene}N_4)$, 58815-31-9; $Ni^{II}(Me_2\text{pyo}[14]\text{triene}N_4)$, 47023-91-6; $Co^{II}(Me_2\text{pyo}[14]\text{triene}N_4)$, 57066-20-3; $Co^{II}([15]aneN_4)$, 87533-24-2; $Ni^{II}(Me_2[14]4,11\text{-diene}N_4)$, 34679-84-0; $Ni^{III}(Me_2[14]4,11\text{-diene}N_4)$, 87533-26-4; $Ni^{II}(Me_2[14]4,7\text{-diene}N_4)$, 46754-95-4; $Ni^{III}(Me_2[14]4,7\text{-diene}N_4)Cl$, 87533-30-0; $Ni^{II}(Me_6[14]1,4,8,11\text{-tetraene}N_4)$, 18444-46-7; $Ni^{II}(Me_6[14]aneN_4)$, 18444-42-3; $Fe(phen)_3{}^{3+}$, 13479-49-7; $Co(OH_2)_6{}^{3+}$, 15275-05-5; $Ru(bpy)_3{}^{3+}$, 18955-01-6; $Ru(bpy)_3{}^{2+}$, 15158-62-0; $Co(OH_2)_5Cl^{2+}$, 83862-38-8; $Fe(OH_2)_6{}^{2+}$, 15365-81-8; Cl^-, 16887-00-6; $Cl_2{}^-$, 12595-89-0.

Supplementary Material Available; Tables of kinetic and electrochemical data (23 pages). Ordering information is given on any current masthead page.