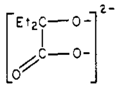
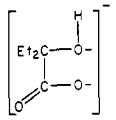
Table I. Magnetic Moments of Some Chromium Complexes[a]

complex	source	μ_{eff}, μ_B
$Cr(H_2O)_6^{3+}$		3.9
$[(Lig)_2Cr^VO]^-$ [b] (I)	$Na_2Cr_2O_7 + Et_2C(OH)COOH$[1]	1.9
$[(HLig)Cr^{III}(H_2O)_4]^{2+}$ [c]	$[(Lig)_2Cr^VO]^- + N_2H_4$[2]	3.5
$(HLig)_2Cr^INO(H_2O)$ (II)	$[(Lig)_2Cr^VO]^- + NH_2OH$[d]	2.3
$(HLig)Cr^INO(H_2O)_3^+$	$[(Lig)_2Cr^VO]^- + NH_2OH$[e]	2.6
$[Cr^I(H_2O)_5NO]^{2+}$	$Cr(H_2O)_6^{2+} + NO$[5]	2.2[f]

[a] Measured in solution at 293 K, by using the procedure of Evans.[7] [b] Lig =



[c] HLig =



[d] Principal product when reaction is carried out with a 27-fold excess of ligand. [e] Principal product when reaction is carried out with a 4-fold excess of ligand; products separated by cation-exchange chromatography (see text). [f] Reference 6.

by strong metal-to-ligand back-bonding.[10]

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Registry No. I, 75476-70-9; II, 83207-89-0; NH_2OH, 7803-49-8.

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(10) See, for example: Johnson, B. F. G.; McCleverty, J. A. *Prog. Inorg. Chem.* **1966**, *7*, 277.

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Oxidation-Reduction Reactions of Complexes with Macrocyclic Ligands. Electronic Requirements of Inner-Sphere Electron-Transfer Pathways[1]

Sir:

Reactivity patterns in those transition metal complex reactions in which transfer of a bridging ligand accompanies electron transfer[2] are poorly understood.[3,4] This is in contrast to the relatively sophisticated level of understanding of reactivity patterns in simple outer-sphere electron-transfer reactions.[3,5-9] Again in contrast to outer-sphere reactions, for which free energy dependencies are reasonably well established and for which there is a great deal of information about free energy independent reactivities,[3,5-9] most of the available information about inner-sphere reactions is complicated by unknown (sometimes indeterminable) contributions of the free energy change accompanying electron transfer.

We have been examining the inner-sphere electron-transfer reactions of complexes containing macrocyclic ligands.[10] In such systems it is often possible to determine self-exchange rate constants and/or cross-reaction rate constants and equilibrium constants for inner-sphere reaction pathways. A number of features of the information acquired about free energy independent inner-sphere reactivities has led us to postulate that many aspects can be usefully described, taking account of the homolytic bond-breaking/bond-making process across the reaction coordinate, in terms of a three-center (M–S–M′) transition-state bonding interaction.[10b,c] We have now found that inner-sphere reaction rates are appropriately sensitive to the number of electrons present in the orbitals used in the formal transition-state bonding arrangement. In addition, orthogonality of the three-center-bonding orbital and the electron-transfer donor–acceptor orbital appears eliminate the kinetic advantage of the inner-sphere pathway.

We have been investigating the oxidation–reduction reactions of $Ni^{III,II}(N_4)$ and $Cu^{III,II}(N_4)$ couples (N_4 = a 14-membered, tetraaza macrocyclic ligand). These couples are strongly oxidizing, but good-quality cyclic voltammometric data may often be obtained in strongly acidic aqueous solutions (Table I), and in a few cases the oxidized complexes may be generated electrochemically, or chemically, and persist in very acidic solutions for periods up to a few hours (Table I and ref 11). In some of the systems and media studied, the oxidized complexes are known only as short-lived transients generated in flash photolysis experiments.

We have been examining several reactions of the Ni(III)–Ni(II) and Cu(III)–Cu(II) couples, but in this report we wish to emphasize the constrasts in $Co(OH_2)_6^{3+}$ and $Co(OH_2)_5Cl^{2+}$ oxidations of the $M^{II}(N_4)$ complexes:

$$Co(OH_2)_5Cl^{2+} + M^{II}(N_4) \xrightarrow{H_2O} Co(OH_2)_6^{2+} + M^{III}(N_4)Cl \quad (1)$$

The results, summarized in Table I, illustrate what may be general features of the inner-sphere reaction pathway. Some of the complementary information obtained with other reagent combinations is also presented in Table I. Both rate patterns and spectra of the oxidation products of $Ni^{II}(N_4)$ complexes indicate that Cl^--bridged inner-sphere reaction pathways do occur. Oxidations of $Cu^{II}(N_4)$ complexes give products at equilibrium with solvent species even on the flash photolysis time scale, and neither rate patterns nor product spectra distinguish between outer-sphere and inner-sphere pathways for reactions of these copper complexes.

The inner-sphere and outer-sphere rate constants, k^{IS} and k^{OS}, have been found to span very large ranges. As a measure of the deviations of observed rates, from those expected for outer-sphere reaction pathways, it is useful to consider the

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(1) Partial support of this research by the National Institutes of Health (Grant AM 14341) and the National Science Foundation (Grant CHE 80-05497) is gratefully acknowledged.

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Table I. Contrasts in the Outer-Sphere, $Co(OH_2)_6^{3+}$ (k^{OS}), and Potentially Inner-Sphere, $Co(OH_2)_5Cl^{2+}$ (k^{IS}), Reactivity of $M^{II}(N_4)$ Complexes

reductant	E_f,[a] V	k^{OS},[b] $M^{-1}\ s^{-1}$	k^{IS},[c] $M^{-1}\ s^{-1}$	$(k^{IS}/k^{OS})_{\Delta G^\circ \to 0}$	transition-state bonding[e]	donor orbital
$Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$	0.564[f]	1×10	1.6×10^6 [g]	$\geq 2.5 \times 10^5$	3c-3e	d_{z^2}
$Co(Me_4[14]\text{tetraene}N_4)(OH_2)_2^{2+}$	0.564[f]	2.2×10^2	1.5×10^7 [g]	$\geq 7 \times 10^4$	3c-3e	d_{z^2}
$Ni(Me_6[14]4,11\text{-diene}N_4)^{2+}$	1.34 (1 M $HClO_4$)	1.4×10^2	7.9×10^5	9×10^3	3c-4e	d_{z^2}
$Ni([14]\text{ane}N_4)^{2+}$	1.03 (1.5 M $HClO_4$)	8.6×10	5.3×10^7	2.2×10^5	3c-4e	d_{z^2}
$Ni(Me_4[14]\text{tetraene}N_4)^{2+}$	1.26 (6 M $HClO_4$)[h]	5.0×10	1.6×10^5	$\sim 3 \times 10^4$ [i]	3c-4e	d_{z^2}
$Cu([14]\text{ane}N_4)^{2+}$	~1.3 (1 M $HClO_4$)[j]	2.8×10^3	$\sim 4.0 \times 10^3$	~4	3c-4e	$d_{x^2-y^2}$
$Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$ (with $Co^{III}(Me_4[14]\text{tetraene}N_4)(OH_2)Cl$)		1.3×10^{-3} [k]	1.5×10^3 [l]	2×10^6	3c-3e	d_{z^2}
$Ni([14]\text{ane}N_4)^{2+}$ (with $Ni^{III}(Me_6[14]4,11\text{-diene}N_4)Cl$)		6×10^3	4×10^6	1.5×10^2	3c-5e	d_{z^2}
$Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$ (with $Ni^{III}([14]\text{ane}N_4)Cl$)		7.6×10^2	3.1×10^6 [g]	$\geq 1.5 \times 10^4$	3c-4e	d_{z^2}

[a] Vs. NHE; 25 °C; this work, except as indicated; medium indicated in parentheses. [b] Rates of $Co(OH_2)_6^{3+}$ reactions have been determined as a function of H^+; values cited are limits for $[H^+]^{-1} \to 0$; 25 °C; ionic strength 3 M. [c] $Co(OH_2)_5Cl^{2+}$ was generated by means of the Cl_2^-–$Co(OH_2)_6^{2+}$ reactions; see ref 10a. The $Co(N_4)(OH_2)Cl^{2+}$ complex has been generated separately.[10a] $Ni(N_4)Cl^{2+}$ was generated by means of the $Ni(N_4)^{2+}$–Cl_2^- reactions in chloride media. [d] Corrected for the differences in M–Cl formation constants. [e] Based on $M^{II}(N_4)$ d_{z^2}, ·X p_z, and Co^{II} d_{z^2}. [f] Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* 1979, *101*, 1131. [g] Rate may be limited by water substitution on $Co^{II}(N_4)$.[10a] [h] Value based on the equilibrium constant for $Ni(N_4)^{2+} + Ru(bpy)_3^{3+} \rightleftharpoons Ni(N_4)^{3+} + Ru(bpy)_3^{2+}$; 25 °C, 1 M $HClO_4$ and $E_f = 1.26$ V vs. NHE for the ruthenium couple. [i] Uncorrected value; no formation constant for $Ni(Me_4[14]\text{tetraene}N_4)Cl^{2+}$ is available. [j] Estimated value based on electron-transfer rates. [k] Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* 1981, *103*, 1431. [l] Reference 10a.

ratios k^{IS}/k^{OS}. In order to be a measure of the intrinsic (or free energy independent) rate advantage of the inner-sphere pathway, this ratio must be extrapolated to $\Delta G^\circ = 0$. For present purposes an approximate extrapolation has been obtained on the basis of the assumption of similar dependencies of the inner-sphere[10] and outer-sphere reactions on ΔG° and with correction for differences in M–Cl formation constants.[12]

Values of $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0}$ seem to run the range 10^6–10^7 for Co(III)–Co(II) couples.[10a] While the corresponding inner-sphere reactions are complicated by water substitution on $Co(N_4)(OH_2)_2^{2+}$, a comparable ratio of reactivity is seen for the $Co(OH_2)_5Cl^{2+}$ and $Co(OH_2)_6^{3+}$ oxidations of cobalt substrates. Smaller values are found for the oxidations of $Ni(N_4)^{2+}$ substrates: the geometric mean of values in Table I is $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0} \approx 4 \times 10^4$. A very similar value of $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0}$ is found for the $Ni^{III}([14]\text{ane}N_4)Cl$ oxidation of $Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{3+}$, consistent with the interpretation that this quantity reflects the electronic composition of the Cl^--bridged transition state and is not inordinately sensitive to the details of assembling this transition state. To the extent that $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0}$ is a measure of the intrinsic kinetic advantage of the inner-sphere pathway, and to the extent that these intrinsic reactivities may be partitioned into separate donor and acceptor contributions, analogous to the outer-sphere electron-transfer limit,[5] the ratio found for Co–Ni reactions should be approximately a geometric mean of the intrinsic inner-sphere rate advantage for Co–Co and Ni–Ni couples. Thus, from the Co–Ni cross reactions one would infer $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0} \simeq 10^2$ for Ni–Ni couples, and this is in accord with the relatively small inner-sphere rate advantage found for the $Ni(Me_6[14]4,11\text{-diene}N_4)Cl^{2+}$–$Ni([14]\text{ane}N_4)^{2+}$ reaction (Table I). Finally, we find essentially no rate advantage for the inner-sphere pathway, involving axial bridging, in the low-spin Cu(III)–Cu(II) couple.

These observations may be summarized as follows: (1) The effectiveness of the inner-sphere pathway in σ^*–σ^* exchanging systems decreases as the number of electrons in the bridging (or three-center bonding) interaction is increased. (2) The inner-sphere pathway has a significant kinetic advantage only if the transition-state bonding interaction strongly mixes the electron-transfer donor and acceptor orbitals.

Registry No. $Co(OH_2)_6^{3+}$, 15275-05-5; $Co(OH_2)_5Cl^{2+}$, 17712-88-8; $Co(Me_6[14]4,11\text{-diene}N_4)(OH_2)_2^{2+}$, 38331-68-9; $Co(Me_4[14]\text{tetraene}N_4)(OH_2)_2^{2+}$, 38337-82-5; $Ni(Me_6[14]4,11\text{-diene}N_4)^{2+}$, 18444-38-7; $Ni([14]\text{ane}N_4)^{2+}$, 46365-93-9; $Ni(Me_4[14]\text{tetraene}N_4)_2^{+}$, 53277-06-8; $Cu([14]\text{ane}N_4)_2^{+}$, 52304-87-7; $Co^{III}(Me_4[14]\text{tetraene}N_4)(CH_2)Cl^{2+}$, 69972-17-4; $Ni^{III}(Me_6[14]4,11\text{-diene}N_4)Cl^{2+}$, 82871-90-7; $Ni^{III}([14]\text{ane}N_4)Cl^{2+}$, 6619-96-0.

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(12) A simple, free energy cycle shows that the difference in ΔG° for eq 1 and the outer-sphere equivalent, $Co(OH_2)_6^{3+}$–$M^{II}(N_4)$, can be attributed to the difference in formation constants of $Co(OH_2)_5Cl^{2+}$ and $M^{III}(N_4)Cl$. Correction for this factor, assuming a square root dependence of the rate constant on the equilibrium constant,[10a,13,14] takes the form of the ratio of the formation constants. Values of k^{IS}/k^{OS} have been multiplied by $[K(M(N_4)Cl^{2+})/K(CoCl^{2+})]^{1/2}$ to effect this correction. The more "correct equivalent" outer-sphere reference reaction would be the outer-sphere rate for $Co(OH_2)_5Cl^{2+}$–$M^{II}(N_4)$. We estimate that this choice would not increase $(k^{IS}/k^{OS})_{\Delta G^\circ \to 0}$ by as much as a factor of 10. We did not make corrections for any differences in work terms.

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