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Examination of the Intrinsic Barrier to Electron Transfer in Hexaaquocobalt(III): Evidence for Very Slow Outer-Sphere Self-Exchange Resulting from Contributions of Franck–Condon and Electronic Terms[1]

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Rates of the $Co(OH_2)_6^{3+}$ oxidations of $M(N_4)(OH_2)_2^{2+}$ (N_4 = a tetraaza macrocycle, M = Co, Ni), $Co(sepulchrate)^{2+}$, and $Ru(NH_3)_4phen^{2+}$ have been determined. These observations have been combined with data from several previous studies to demonstrate that the free energy dependence of the rate constants of $Co(OH_2)_6^{3+}$ reactions is well represented by the classical Marcus expression. However, this correlation leads to an intrinsic parameter applicable to the outer-sphere cross reactions involving the $Co(OH_2)_6^{3+,2+}$ couple, $\Delta G_i^{\ddagger}(Co) \approx 132$ kJ mol^{-1}, which is much greater than that obtained directly from the $Co(OH_2)_6^{3+,2+}$ self-exchange, 58 kJ mol^{-1}. This observed cross-reaction behavior is very similar to that of the closely related $Co(NH_3)_6^{3+,2+}$ couple. Similar structural differences between Co(III) and Co(II) found in both couples dictate comparable and large contributions of Franck–Condon factors to the $Co(NH_3)_6^{3+,2+}$ and $Co(OH_2)_6^{3+,2+}$ outer-sphere self-exchange reactions. In fact, the reported value for the $Co(OH_2)_6^{3+,2+}$ self-exchange rate constant is nearly 10^6 times larger than the rate constant based only on Franck–Condon factors. For both Co(III)/Co(II) couples there appears to be a smaller, but significant electronic (or nonadiabatic) contribution to rate. The larger intrinsic reactivity associated with the $Co(OH_2)_6^{3+,2+}$ self-exchange reaction than with the outer-sphere cross reactions involving this couple must be a consequence of a difference in mechanistic pathway: a water-bridged inner-sphere pathway is proposed for the former. It is noted that the water-bridged inner-sphere pathway is only plausible for a very strong oxidant.

Introduction

The level of understanding of simple outer-sphere electron-transfer reactions has advanced considerably during the past 20 years.[2] To a significant extent this is owing to the systematic separation of the "intrinsic" and free energy dependent components of reactivity. Most often this separation is accomplished by using a formalism proposed by Marcus.[3] The intrinsic barrier to electron transfer thus obtained may then be discussed in terms of various theoretical models. Most models of these intrinsic barriers, $\Delta G_i^{\ddagger}$, to electron transfer treat separately the Franck–Condon parameters, which result from solvent reorganization and from metal–ligand bond length changes, and the purely electronic factors, which result from changes in spin multiplicity or the effects of orbital symmetry or overlap.[3–5] The rate constant for electron transfer may be represented with semiclassical[5,6]

$$k_i(C) = \kappa_{el}\Gamma Z e^{-\Delta G_i^{\ddagger}/RT}$$

or quantum mechanical formulations[4,7]

$$k_i(Q) = N_0\Sigma \langle V_{if} \rangle G(FC)$$

The semiclassical and quantum approaches seem to give comparable results for reactions of transition-metal complexes at room temperature.[5] Very simple models seem to work well for couples involving only very small differences in bond lengths.[8] Somewhat more complex models have evolved for couples such as $Fe(OH_2)_6^{3+,2+}$,[5] where the donor and acceptor orbitals are approximately π nonbonding and bond lengths changes are moderate.[9] The free energy dependencies of cross reactions involving couples such as these are adequately[2,10] represented by the Marcus[3] relation[11] (eq 1) (provided $|\Delta G_{ab}^{\circ}| < \lambda_{ab}$).

$$\Delta G_{ab}^{\ddagger} = w_{ab} + \frac{\lambda_{ab}}{4}\left(1 + \frac{\Delta G_{ab}^{\circ}}{\lambda_{ab}}\right)^2 \qquad (1)$$

In view of the success of the simple models and eq 1 in describing a large number of electron-transfer reactions, it has seemed surprising that reactions involving cobalt(III)/cobalt(II) couples have often exhibited exceptional behavior.[2,10,12,13] It has been suggested[4,12g] that a part of the observed complexity must arise from the electronic term (i.e., $\langle V_{if} \rangle$ or κ_{el}). Even among electron-transfer reactions of cobalt complexes, the reductions of $Co(OH_2)_6^{3+}$ have been unusual in their peculiarities.[2,13] Thus, the $Co(OH_2)_6^{3+}$ self-exchange

(1) Partial support of this work by the National Institute of Health (Grant AM14341) is gratefully acknowledged.

(2) For recent reviews see: (a) Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic Press: New York, 1970. (b) Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem..,* *Ser. One* **1971,** *9,* 303. (c) Linck, R. G. *Int. Rev. Sci.: Inorg. Chem., Ser. Two* **1974,** *9,* 173. (d) Linck, R. G. *Surv. Prog. Chem.* **1976,** *7,* 89. (e) Sutin, N. in "Tunneling in Biological System"; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schreiffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1979; p 201. (f) Scott, K. L. *Inorg. React. Mech.* **1976,** *4,* 5. (g) Cannon, R. D. *ibid.* **1978,** *5,* 3. (h) Cannon, R. D. *Ibid.* **1979,** *6,* 3.

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

(4) (a) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975,** *63,* 4358. (b) Kestner, N. R.; Logan, J.; Jortner, J. *J. Phys. Chem.* **1974,** *78,* 2148. (c) Jortner, J., Ulstrup, J., *J. Am. Chem. Soc.* **1979,** *101,* 3744. (d) Buhks, E.; Bixon, M.; Jortner, J.; Navon, G. *Inorg. Chem.* **1979,** *18,* 2014.

(5) (a) Brunschwig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980,** *102,* 5798. (b) Newton, M. D. *Int. J. Quantum Chem. Quatum Chem. Symp.* **1980,** *No. 14,* 363.

(6) Where κ_{el} is a transmission coefficient, Γ is a tunnelling correction, and Z is a bimolecular collision rate (usually set equal to 10^{11} M^{-1} s^{-1}).

(7) Where N_0 is a normalizing constant, the summation is over all nuclear configurations and electronic states, $\langle V_{if} \rangle$ is a two-center electron exchange integral, and $G(FC)$ is the nuclear or Franck–Condon factor.

(8) Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979,** *101,* 883.

(9) Sham, F. K.; Hastings, J. B.; Perlman, M. L. *J. Am. Chem. Soc.* **1980,** *102,* 5904.

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

(11) In eq 1, $\lambda/4$ is equivalent to $\Delta G_i^{\ddagger}$ in the preceding discussion; w_{ab}^R is a work term (mostly Coulombic), and we have assumed $w_{ab} = w_{ba}$ (similar work terms for reactants and products).

(12) (a) Liteplo, M. P.; Endicott, J. F. *Inorg. Chem.* **1971,** *10,* 1420. (b) Rillema, D. P.; Endicott, J. F.; Patel, R. C. *J. Am. Chem. Soc.* **1972,** *94,* 394. (c) Rillema, D. P.; Endicott, J. F. *Inorg. Chem.* **1972,** *11,* 2361. (d) Rillema, D. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1972,** *94,* 8711. (e) Rillema, D. P.; Endicott, J. F.; Kane-Maguire, N. A. P. *J. Chem. Soc., Chem. Commun.* **1972,** 495. (f) Rillema, D. P.; Endicott, J. F. *Inorg. Chem.* **1976,** *15,* 1459. (g) 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. (h) Durham, B.; Endicott, J. F.; Wong, C.-L.; Rillema, D. P. *Ibid.* **1979,** *101,* 847.

(13) (a) Davies, G.; Warnqvist, B. *Coord. Chem. Rev.* **1970,** *5,* 349. (b) Bodek, I; Davies, G. *Ibid.* **1974,** *14,* 269. (c) Davies, G. *Ibid.* **1974,** *14,* 287.

Table I. Kinetic Data for $Co(OH_2)_6^{3+}$ Reactions

reductant	$10^4 \times$ [reductant], M	$10^4 \times$ [Co(OH$_2$)$_6$$^{3+}$],[a] M	E^f,[b] V	T, °C	k_{ab},[c] M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} deg^{-1}
Co(Me$_2$[14]4,7-dieneN$_4$-6-one)(OH$_2$)$_2$$^{2+}$	~0.5–1	2.5–5.8 (6)	0.600	25	384 ± 21		
Co(Me$_2$pyo[14]trieneN$_4$)(OH$_2$)$_2$$^{2+}$	~1	7.1 (2)	0.567	25	480 ± 20		
Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$	~0.5–1	2.2–5.8 (6)	0.564	25	337 ± 23	50 ± 2	−25 ± 50
		2.4–4.3 (4)		18	175 ± 5		
		2.4–4.3 (4)		10	105 ± 4		
Co(Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)$_2$$^{2+}$	5	50	0.564	25	66 ± 10		
Co([14]aneN$_4$)(OH$_2$)$_2$$^{2+}$	0.5	2.8–13.8 (9)	0.421	25	700 ± 75		
Co([15]andN$_4$)(OH$_2$)$_2$$^{2+}$	10.0	33–160 (20)	0.655^d	25	257 ± 21		
Co(sep)$^{2+}$	0.5	2.25–11.0 (9)	−0.30	25	700 ± 77		
Ru(NH$_3$)$_4$(phen)$^{2+}$	0.10	0.56–3.37 (12)	0.515	25	(4.0 ± 0.1) × 10^4		
Ni(Me$_6$[14]4,11-dieneN$_4$)$^{2+}$ ^{e}	1.0	17–85 (20)	1.34^d	25	280 ± 16		
Ni([14]aneN$_4$)$^{2+}$ ^{e,f}	0.16	(2.03–27.08)	1.03^d	25	642 ± 94		

^{a} Range of values. Number of determinations is given in parentheses. ^{b} On the basis of ref 46. ^{c} 3 M HClO$_4$ except as indicated. ^{d} Kumar, K.; Endicott, J. R., work in progress. ^{e} 1.5 M HClO$_4$. ^{f} Reference 31.

rate[14] is 5 M^{-1} s^{-1}; this is much larger than the classically predicted rate,[15–18] and the cross reactions are always too slow by several orders of magnitude.[2,10,13,19–22] There have even been suggestions that some inherent property of the Co-(OH$_2$)$_6$$^{3+,2+}$ couple causes the cross reactions to approach a limiting rate and to deviate dramatically from behavior predicted by eq 1. These suggestions stand in striking contrast to the results of our studies of electron-transfer reactions involving low-spin Co(N$_4$)(OH$_2$)$_2$$^{3+,2+}$ couples (N$_4$ = a tetraaza macrocyclic ligand), for which we have found that (1) provides an excellent accounting of the free energy dependence of the rate constants.[12]

Perhaps even more striking is the contrast in self-exchange rate behavior of the Co(OH$_2$)$_6$$^{3+,2+}$ and Co(NH$_3$)$_6$$^{3+,2+}$ couples. While the respective ions are similar in size, charge, and spin characteristics, the reported self-exchange rates of these couples differ by a factor of more than 10^{10}.[14,23]

We have undertaken some additional studies of the electron-transfer reactivity of the Co(OH$_2$)$_6$$^{3+,2+}$ couple in the hope of gaining some new insight into the source of the deviations from expected behavior. These new studies have utilized as counterreagents a number of redox couples for which self-exchange and thermochemical information have becomes available in recent years. One would anticipate in these studies

(14) Habib, H. S.; Hunt, J. P. *J. Am. Chem. Soc.* **1966**, *88*, 1668.

(15) With use of the classical harmonic oscillator approach to estimate the Franck-Condon term,[2e] $\Delta G_i^* = {}^6/_2 (f_{II}f_{III}/(f_{II} + f_{III}))\Delta X^2 \simeq 66$ kJ mol^{-1}, quantization of the vibrations[4] would result in a somewhat smaller value of ΔG_i^*.[5] Other terms contributing[2–5,8] to ΔG_i^*(FC) are a Coulombic work term and solvent reorganization, $w \simeq 4$ kJ mol^{-1} and $\Delta G_{out}^* \simeq 30$ kJ mol^{-1}, respectively, for ions of this size.[8] These quantities would result in a rate constant (assuming $\kappa_{el} \simeq 1$) $k \simeq 2 \times 10^{-7}$ M^{-1} s^{-1}. In obtaining this estimate we have used as force constants $f_{II} \simeq 119$ N m^{-1} (based on the Co^{II}–OH$_2$ bond length and a correlation discussed in ref 12g) and $f_{III} \simeq 263$ N m^{-1} [16] and bond lengths d(Co^{II}–OH$_2$) = 209 pm[17] and d(Co^{III}–OH$_2$) = 1.91 pm[18] for cobalt(II) and cobalt(III), respectively. See also Table V.

(16) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970.

(17) Cobalt(II)–water bond lengths have been found to vary from 208 to 210 pm in Co(OH$_2$)$_6$$^{2+}$ salts: McCandish, E. F.; Michael, T. K.; Neal, J. A.; Lingafelter, E. C.; Rose, N. J. *Inorg. Chem.* **1978**, *17*, 1383. On the basis of EXAFS data, the Co^{II}–OH$_2$ bond length in aqueous solution has been reported to be 208 pm: Morrison, T. I.; Reis, A. H., Jr.; Gebert, E.; Iton, L. E.; Stucky, G. D.; Suib, S. L. *J. Chem. Phys.* **1980**, *72*, 6276.

(18) The Co^{III}–OH$_2$ bond length is taken as 191 pm based on the X-ray crystal structure of Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2$$^{3+}$.[12a]

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

(20) Davies, G. *Inorg. Chem.* **1971**, *6*, 1155.

(21) Hyde, M. R.; Davies, R.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 1838.

(22) Ekstrom, A.; McLaren, A. B.; Smythe, L. E. *Inorg. Chem.* **1975**, *12*, 2899.

(23) (a) Stranks, D. R. *Discuss. Faraday Soc.* **1960**, *29*, 73. (b) Birader, N. S.; Stranks, D. R.; Vaidya, M. S. *Trans. Faraday Soc.* **1962**, *58*, 2421.

Table II. pH Dependence of Some Co(OH$_2$)$_6$$^{3+}$ Reactions

reductant	range of^a [H$^+$], M	$k_{obsd} = k_I + k_{II}/[H^+]$[b] k_I, M^{-1} s^{-1}	k_{II}, M^{-2} s^{-1}
Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2$$^{2+}$	0.15–3.0 (8)	220 ± 40	448 ± 20
Co(Me$_2$pyo[14]trieneN$_4$)(OH$_2$)$_2$$^{2+}$	0.3–3.0 (7)	346 ± 30	567 ± 20
Co(Me$_6$[14]4,11-dieneN$_4$)(OH$_2$)$_2$$^{2+}$	0.75–3.0 (7)	10 ± 10	255 ± 15
Co([15]aneN$_4$)(OH$_2$)$_2$$^{2+}$	1.2–3.0 (7)	270 ± 20	~0
Co([14]aneN$_4$)(OH$_2$)$_2$$^{2+}$	1.2–3.0 (4)	665 ± 20	~0
Co(sep)$^{2+}$	0.3–3.0 (6)	577 ± 20	~0
Ni(Me$_6$[14]4,11-dieneN$_4$)$^{2+}$	0.3–3.0 (7)	140 ± 60	510 ± 100
Ni([14]aneN$_4$)$^{2+}$ ^{c}	0.63–1.5 (3)	86 ± 43	880 ± 40

^{a} $\mu = 3.0$ M (NaClO$_4$, HClO$_4$) except as indicated (25 °C). Number of determinations is given in parentheses. ^{b} Least squares fit of data. Corrections for activity variations have been applied (see supplementary material). ^{c} $\mu = 1.5$ M (LiClO$_4$, HClO$_4$). Based on least-squares fit of 25 °C data from ref 31.

that deviations from Franck–Condon dictated reactivity patterns of the Co(OH$_2$)$_6$$^{3+,2+}$ couple might be largely attributable to the electronic factor $\langle V_{if} \rangle$, which is very sensitive to the changes in spin multiplicity[4] which must accompany reduction of low-spin Co(OH$_2$)$_6$$^{3+}$ or oxidation of high-spin Co(OH$_2$)$_6$$^{2+}$.

Experimental Section

Reagents. Most macrocyclic complexes were prepared, isolated, and purified as described elsewhere.[12] Solutions of Co([14]-aneN$_4$)(OH$_2$)$_2$$^{2+}$ and Co([15]aneN$_4$)(OH$_2$)$_2$$^{2+}$ were prepared by mixing the ligand with a solution of Co(ClO$_4$)$_2$·xH$_2$O as previously described.[24] Co([15]aneN$_4$)(OH$_2$)$_2$$^{2+}$ was always kept in neutral solution, because it is unstable in acid solution: $k_d = 0.49$ s^{-1} in 0.05 M HClO$_4$ with 0.5 M ionic strength; and $k_d = 0.28$ s^{-1} in 1 M HClO$_4$. The literature method was used for preparation of Ni(Me$_6$[14]-4,11-dieneN$_4$)$^{2+}$.[25]

Solutions of Co(OH$_2$)$_6$$^{3+}$ were prepared by electrolysis of Co-(ClO$_4$)$_2$·xH$_2$O in 3 or 6 M HClO$_4$ at 0 °C;[12] [Co(OH$_2$)$_6$$^{3+}$] was determined from the absorbance of stock solutions at 605 nm (ϵ 35 M^{-1} cm^{-1}). Solutions of Co(sep)$^{2+}$[26] were prepared treating Co(sep)$^{3+}$

(24) Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(25) Tait, A. M.; Busch, D. H. *Inorg. Synth.* **1977**, *18*, 5.

(26) Abbreviations: Me$_4$[14]tetraeneN$_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; Me$_6$[14]4,11-dieneN$_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraaazacyclotetradeca-4,11-diene; [14]aneN$_4$ = 1,4,8,11-tetrazacyclotetradecane; Me$_2$pyo[14]trieneN$_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadeca-1-(17),2,11,13,15-pentaene; Me$_2$[14]4,7-dieneN$_4$-6-one = 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene-6-one; [15]aneN$_4$ = 1,4,8,11-tetraazacyclopentadecane; sepulchrate = (*S*)-1,3,6-8,10,13,16,19-octaazabicyclo[6.6.6]eicosant.

with zinc dust in deaerated solutions. $Co(sep)Cl_3$ was prepared as reported previously.[27] $[Ru(NH_3)_4(phen)](TFMS)_2$ was prepared from $[Ru(NH_3)_5OH_2](TFMS)_3$ with literature procedures.[28,29] $[Ru(NH_3)_6]Cl_3$ was obtained from Matthey-Bishop.

Solutions of $Ni^{III}(N_4)$ complexes were obtained from Ce(IV) oxidations of acidic solutions of $Ni^{II}(N_4)$. The Ni(II) complexes were prepared from free macrocyclic ligands and nickel (II) acetate.[25] Conversion to $Ni^{III}(N_4)$ was confirmed by comparison of product spectra to those reported previously.[30-32] Nickel(III) solutions thus prepared were stable for several hours.
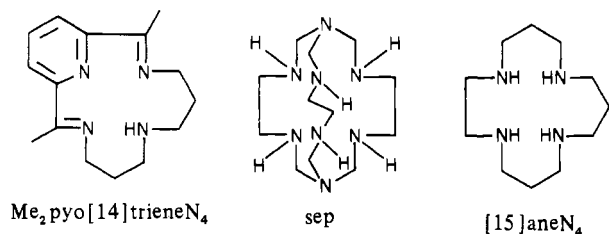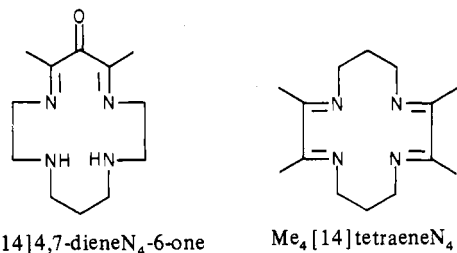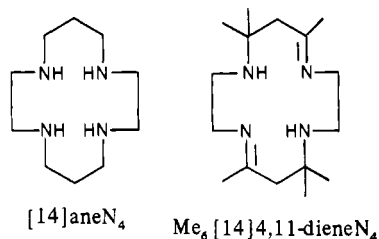
Solutions of reducing agents were deaerated by purging with a stream of Cr^{2+}–scrubbed N_2 or Ar. Trifluoromethanesulfonic acid (HTFMS) was distilled at least twice before use. The sodium salt, NaO_3SCF_3, was prepared by the reaction of HO_3SCF_3 and Na_2CO_3. Ionic strength was generally adjusted with NaO_3SCF_3. Deionized, redistilled water was used for all solutions.

Kinetic Apparatus and Methods. Rate constants were determined from changes in absorbance monitored with either a thermostated Gibson-Durrum or Aminco stopped-flow apparatus. All $Co(OH_2)_6^{3+}$ reactions were run in 3 M $HClO_4$.

All reactions were run under pseudo-first-order conditions. Values of k_{obsd} were obtained from the slope of log $(A_\infty - A_t)$ vs. time. Second-order rate constants were obtained from the slope of k_{obsd} vs. concentration of excess reagent.

Results

All the $Co(OH_2)_6^{3+}$ oxidations were studied with $[Co^{3+}]$ in large excess. The results of these studies are presented in Table I. We have also investigated the dependence of several of the cross reactions on $[H^+]$ in the range 0.1 M $\leq [H^+] \leq$ 3 M. We found the $Co(OH_2)_6^{3+}$ oxidations of $Co(sep)^{2+}$, $Ru(NH_3)_4phen^{2+}$, $Co([14]aneN_4)(OH_2)_2^{2+}$, and $Co([15]$-

[14]aneN$_4$

Me$_6$[14]4,11-dieneN$_4$

Me$_2$[14]4,7-dieneN$_4$-6-one

Me$_4$[14]tetraeneN$_4$

Me$_2$pyo[14]trieneN$_4$

sep

[15]aneN$_4$

aneN$_4$)(OH$_2$)$_2^+$ to be pH independent over the range of $[H^+]$ investigated. Several other reactions were found to be pH dependent, and their pH dependence is summarized in Table II; the kinetic details may be found in Table S-I.[33] In each
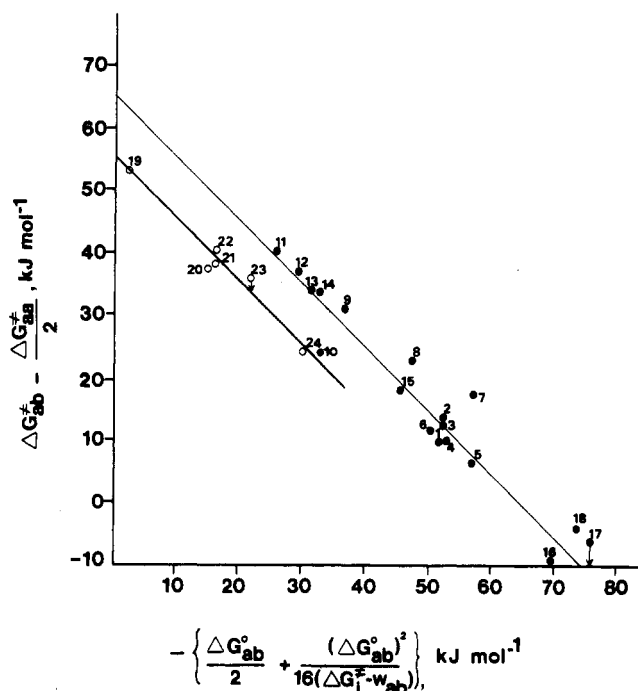
(27) Ferraudi, G. J.; Endicott, J. F. *Inorg. Chim. Acta* **1979**, *37*, 219.
(28) Stanbury, D. M.; Hass, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518.
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(30) Olson, D. C.; Vasilavskis, J. *Inorg. Chem.* **1969**, *8*, 1611.
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(32) Lovecchio, F. V.; Gore, E. S.; Busch, D. M. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

Figure 1. Free energy dependence of the rate constant for reduction of $Co(OH_2)_6^{3+}$ (closed circles) and $Co(NH_3)_6^{3+}$ (open circles). The reactions involved are indicated by the code numbers in Table IV. See Table IV for conditions and values of parameters. Quadratic terms of the free energy dependence were calculated from values of $\Delta G_{bb}^* = \Delta G^*(FC)$ from Table V.

Table III. Self-Exchange Rate Constants and Potentials for Some Couples Estimated from Cross Reactions[a]

couple	medium	E_a^f, V	k_{aa}, $M^{-1} s^{-1}$
Ni([14]andN$_4$)$^{3+,2+}$	1.5 M HClO$_4$	1.03	1.2×10^3
Ni(Me$_6$[14]4,11-dieneN$_4$)$^{3+,2+}$	1.5 M HClO$_4$	1.34	6
Co([15]aneN$_4$)(OH$_2$)$_2^{3+,2+}$	0.1 M HClO$_4$	0.65	6.0×10^{-3}

[a] Kumar, K.; Endicott, J. F., work in progress. Based on oxidations of $M(N_4)^{2+}$, reductions of $M(N_4)^{3+}$ with reagents of known E_b° and k_{bb}. The best fit of these data to $k_{ab} = (k_{aa}k_{bb}K_{ab}f_{ab})^{1/2}$ was obtained in order to estimate E_a° and k_{aa}.

case, the pH dependence is well fitted to $k_{obsd} = k_I + k_{II}'/[H^+]$. We interpret the acid-independent pathways, k_I, to correspond to the outer-sphere $Co(OH_2)_6^{3+}$ oxidations of the $M^{II}(N_4)$ complexes. The acid dependence can be attributed to the $CoOH^{2+}/M^{II}(N_4)$ reaction. It is the values of k^I which have been included in Figure 1.

The self-exchange rate constants and standard potentials have not been reported for the $Ni^{III,II}([14]aneN_4)$, $Ni^{III,II}$-$(Me_6[14]4,11-dieneN_4)$, and $Co^{III,II}([15]aneN_4)$ complexes in water. We have estimated these parameters as the best fits to the Marcus square-root relation of the kinetic parameters for $Fe(phen)_3^{3+}$ oxidations of $M^{II}(N_4)$ and $Ru(NH_3)_6^{2+}$ or $Co(sep)^{2+}$ reductions of $M^{III}(N_4)$ for each $M(N_4)$ complex. The resulting self-exchange and E° parameters are presented in Table III. The details of these kinetic studies will be discussed elsewhere.

Discussion

In Table IV we have summarized the information on those $Co(OH_2)_6^{3+}$ and $Co(NH_3)_6^{3+}$ reactions for which we have been able to find the kinetic and thermodynamic information for the correlation in Figure 1.

In order to generate a free energy correlation based on eq 1 which is relatively insensitive to the intrinsic parameters of

(33) Supplementary material. See paragraph at end of paper.

Table IV. Kinetic and Thermodynamic Parameters for Reductions of $Co(OH_2)_6^{3+}$ and $Co(NH_3)_6^{3+}$ [a]

reductants	code no.	E^f [a], V	$-\Delta G_{ab}°$, kJ mol⁻¹	k_{aa}, M⁻¹ s⁻¹	$\Delta G_{aa}^{\ddagger}$, kJ mol⁻¹	k_{ab}, M⁻¹ s⁻¹	w_{aa}, kJ mol⁻¹	$\Delta G_{ab}^{\ddagger}$ [c], kJ mol⁻¹	$\Delta G_{ab}^{\ddagger} - \tfrac{1}{2}\Delta G_{aa}^{\ddagger}$, kJ mol⁻¹	$-\Delta G_{ab}°/2 + (\Delta G_{ab}°)^2/16(\Delta G_1^{\ddagger} - w_{ab})$, kJ mol⁻¹
A. With $Co(OH_2)_6^{3+}$										
$Co(Me_2[14]4,7\text{-dieneN}_4\text{-}6\text{-one})(H_2O)_2^{2+}$	1	0.600	128	4.4×10^{-3} d	76	384 e	4.4	48	10	51.9
$Co(Me_2pyo[14]trieneN_4)(OH_2)_2^{2+}$	2	0.567	131	0.093 d	60	346 e,f	4.4	48	14	52.2
$Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$	3	0.564	131	0.050 d	70	220 e,f	4.4	48.3	13.2	52.3
$Co(Me_6[14]4,11\text{-dieneN}_4)(OH_2)_2^{2+}$	4	0.564	131	4.5×10^{-5} d	87	10 e,f	4.4	~57	~10	53.4
$Co([14]aneN_4)(OH_2)_2^{2+}$	5	0.421	145	8.0×10^{-4} d	81	665 e	4.4	46.7	6.2	57.3
$Co([15]aneN_4)(OH_2)_2^{2+}$	6	0.655 g	124	6.0×10^{-3} g	75	270 e	4.4	48.8	11.3	50.2
$Co(sep)^{2+}$	7	-0.30	156	5 h	59	577 e	6.3	47	17.5	57.6
$Ru(NH_3)_4phen^{2+}$	8	0.515 i	136	3.25×10^6 j	26	4.0×10^4 e	6.3	36	23.3	48.0
$Ni([14]aneN_4)^{2+}$	9	1.03 k	89.4	1.2×10^3 k	41	86 e,f	4.4	51.5	31	36.9
$Ni(Me_6[14]4,11\text{-dieneN}_4)^{2+}$	10	1.34 k	54	6 k	60	120 e,f	4.4	54	24	24
$Fe(5\text{-nitro-phen})_3^{2+}$	11	1.31 l	59.3	2.0×10^9 m	9.6	1.49×10^3 n	3.2	45	40	25.4
$Fe(5\text{-chloro-phen})_3^{2+}$	12	1.18 l	71.8	2.0×10^9 m	9.6	5.0×10^3 n	3.2	42	37	29.6
$Fe(phen)_3^{2+}$	13	1.12 l	77.6	2.0×10^9 m	9.6	1.4×10^4 n	3.2	39	34	31.5
$Fe(5\text{-methyl-phen})_3^{2+}$	14	1.08 l	80.3	2.0×10^9 m	9.6	1.5×10^4 n	3.2	39	34	32.5
$Fe(OH_2)_6^{2+}$	15	0.749	113.3	4.0 o	59	50 p	10	53	23	45.7
$V(OH_2)_6^{2+}$	16	-0.226	207.2	3×10^{-3} q	77	9×10^5 r	10	29	-9.9	69.8
$Cr(OH_2)_6^{2+}$	17	-0.411	225.0	$\leqslant 10^{-5}$ s	>92	1.3×10^4 r	10	39	$\leqslant$-6.4	76.9
U^{3+}	18	-0.626 t	245.8	0.5 u	64	1.1×10^6 r	8	28	-4.0	73.6
B. With $Co(NH_3)_6^{3+}$										
$Ru(NH_3)_6^{2+}$	19	0.06	3.8	4.0×10^3 (0.1) v	38.6 w	0.024 x	10	72.6 w	53.3	1.9
$V(OH_2)_6^{2+}$	20	-0.226	31.4	3×10^{-3} q	77.8 w	1.0×10^{-2} (1.00) bb	10	76.6 w	37.7	14.9
$Cr(bpy)_3^{2+}$	21	-0.26 z	34.7	2×10^9 aa	9.8 w	3.1×10^2 (0.2) bb	3.2	43.6 w	38.6	15.7
$Cr(phen)_3^{2+}$	22	-0.28 z	36.6	2×10^9 aa	9.8 w	3.1×10^2 (0.2) bb	3.2	45.0 w	40.1	16.0
$Cr(OH_2)_6^{2+}$	23	-0.411	49.2	$\leqslant 10^{-5}$ s	$\leqslant$92 w	1.0×10^{-3} (1.0) v	10	82.3 w	$\leqslant$36.3	22.6
U^{3+}	24	-0.626 t	69.9	0.5 u	65.1 w	1.3 cc	8	62.2 w	24.6	30

^{a} All measurements refer to 25 °C, $\mu = 0.5$ (except when different ionic strength is indicated in parentheses; E^f values at $\mu = 0.1$). E^f values based on ref 45 except as indicated. Code numbers identify data plotted in Figure 1. Estimates of Coulombic work terms based on size and ref 8. Values vs. NHE. ^{b} With $E^f = 1.92$ V for $Co(OH_2)_6^{3+,2+}$. ^{c} Based on $k_{aa} = 10^{11} \exp(-\Delta G_{aa}^{\ddagger}/RT)$ or $k_{ab} = 10^{11} \exp(-\Delta G_{ab}^{\ddagger}/RT)$. ^{d} Reference 12g. ^{e} This work. $^f k_{ab}$ is for reaction of $Co(H_2O)_6^{3+}$, calculated from hydrogen ion dependence of rate constants. ^{g} Kumar, K.; Endicott, J. F., work in progress. ^{h} Creaser, I. I.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Springborg, J.; Gene, R. J.; Snow, M. R. *J. Am. Chem. Soc.* 1977, *99*, 3181. ^{i} In ref 10 the redox potential of $Ru(NH_3)_4(bpy)^{3+,2+}$ is given 0.51 while in ref 8 the ΔE of $Ru(NH_3)_4phen^{3+/2+} - Ru(NH_3)_4(bpy)^{3+,2+}$ is 0.005. So the potential of $Ru(NH_3)_4phen^{3+/2+}$ is 0.515 V vs. NHE. ^{j} Reference 8. ^{k} Kumar, K.; Endicott, J. F., unpublished results. ^{l} Based on ref 19. ^{m} Estimate based on $Ru(bpy)_3^{3+,2+}$ (Young, R. L.; Keene, F. R.; Meyer, T. J. *J. Am. Chem. Soc.* 1977, *99*, 2468). ^{n} Reference 19. ^{o} Silverman, J.; Dodson, R. W. *J. Phys. Chem.* 1952, *56*, 846. ^{p} Bennett, L. E.; Sheppard, J. *J. Phys. Chem.* 1962, *66*, 1275. ^{q} Krishnamurthy, K. V.; Wahl, A. C. *J. Am. Chem. Soc.* 1958, *80*, 5921. ^{r} Reference 21. ^{s} Anderson, A.; Bonner, N. A. *J. Am. Chem. Soc.* 1954, *76*, 3826. ^{t} Reference 45c. ^{u} Value estimated in reference cited in note *t*. ^{v} Meyer, T. J.; Taube, H. *Inorg. Chem.* 1968, *7*, 2369. ^{w} Values corrected to $\mu = 0.5$. ^{x} Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* 1974, *13*, 2647. ^{y} Przstas, T. J.; Sutin, N. *J. Am. Chem. Soc.* 1973, *95*, 5545. ^{z} Brunschweig, B.; Sutin, N. *J. Am. Chem. Soc.* 1978, *100*, 7568. ^{aa} Reference 27. ^{bb} Narusawa, Y.; Kimura, M.; Nakano, K. *Bull. Chem. Soc. Jpn.* 1974, *47*, 2017. ^{cc} Espenson, J. H.; Wang, R. T. *J. Chem. Soc. D* 1970, 207.

Table V. Comparison of Calculated Franck–Condon and Observed Self-Exchange Kinetic Parameters

complex	ω_{alg},[a] cm⁻¹	ΔX,[b] pm	$\Delta G_i^{\ddagger,c}$ kJ mol⁻¹	$\Delta G_0^{\ddagger,d}$ kJ mol⁻¹	w,[d] kJ mol⁻¹	$\Delta G^{\ddagger}(FC)$,[e] kJ mol⁻¹	$\Delta G_{exch}^{\ddagger}(obsd)$, kJ mol⁻¹
Co(NH₃)₆	494(+3)	17.4	46(C)	28	6	80(C)	110[f]
	357(+2)		43(Q)			77(Q)	(≥114)[g]
Co(OH₂)₆	500(+3)		66(C)	30	7	103(C)	132[f]
	361(+2)[h]	20	59(Q)			96(Q)	(58)[i]

[a] Breathing modes of CoL₆³⁺ (+3) and CoL₆²⁺ (+2). Data from: Schmidt, K. H.; Muller, A. *Inorg. Chem.* **1975,** *14,* 2183. Reference 16.
[b] Difference in bond length between Co^III–L and Co^II–L; data from ref 17 and 18, and: Stynes, H. C.; Ibers, J. *Inorg. Chem.* **1971,** *10,* 2304.
[c] For the classical (C) calculation of the first coordination sphere reorganizations barrier see footnote 15. The quantum calculation is based on ref 4d with

$$\Delta G_i^{\ddagger}/RT = \frac{2\omega_{II}\omega_{III}nM(\Delta X^2/\hbar)}{\omega_{II}\coth \nu_{III} + \omega_{III}\coth \nu_{II}}$$

[d] Solvent reorganizational, $\Delta G_0^{\ddagger}$, and work, w, terms based on ref 8. [e] $\Delta G^{\ddagger}(FC) = \Delta G_i^{\ddagger} + \Delta G_0^{\ddagger} + w$. [f] Twice the intercept in Figure 1.
[g] Reference 23. [h] With the assumption ω_{111}/ω_{11} to be the same for Co(NH₃)₆ and Co(OH₂)₆. [i] Reference 14.

the CoL₆³⁺,²⁺ couples, we have recast eq 1 into the form (where the w_{ij} are work terms and we assume $w_{ab} = {}^1/_2[w_{aa} + w_{bb}])$[15]

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

For a wide variety of counter reagents (i.e., aquo ions, macrocycle complexes, polypyridyl complexes, etc.), eq 1 provides a completely adequate description of the free energy dependence of reductions of Co(OH₂)₆³⁺. The previous claims that eq 1 does not correctly correlate Co(OH₂)₆³⁺ [13,20-22] reactions were based on correlations which did not take proper account of the variations in counter reagent intrinsic parameters. Figure 1 demonstrates clearly, as Sutin and co-workers pointed out long ago,[19] that the small values of rate constants for Co(OH₂)₆³⁺ reactions originate in an unexpectedly large value of the intercept of the free energy correlations. Several points are raised by this correlation: (1) there are striking similarities in the outer-sphere electron-transfer behavior of Co(NH₃)₆³⁺,²⁺ and Co(OH₂)₆³⁺,²⁺; (2) there is a huge discrepancy between the Co(OH₂)₆³⁺,²⁺ self-exchange rate constant inferred from eq 2, 10⁻¹²±² M⁻¹ s⁻¹, and the measured self-exchange rate constant, 5 M⁻¹ s⁻¹; (3) there is some ambiguity regarding the value of intrinsic reorganizational parameters for Co(OH₂)₆³⁺,²⁺ to be used in eq 2 for cross-reaction correlations. These three points are in fact very closely related, but each requires separate, careful consideration.

A. Co(OH₂)₆³⁺–Co(NH₃)₆³⁺ Comparison. The similarities in cross-reaction behavior of Co(OH₂)₆³⁺ and Co(NH₃)₆³⁺ are very striking indeed: Figure 1 suggests that even the intrinsic parameters which correlate the cross reactions of these two complexes are somewhat similar: $\Delta G_1^{\ddagger}$(Co) ≃ 132 and 110 kJ mol⁻¹ respectively for the hexaaquo and hexaamine complexes; the implied self-exchange rates are ~10⁻¹² and ~10⁻⁸ M⁻¹ s⁻¹ respectively (μ ≃ 0.5; 25 °C).[15] That both these couples should involve essentially forbidden electron-exchange processes is in accord with naive expectation based on the similarities of their pertinent physical properties: (1) both couples involve high-spin cobalt(II) and low cobalt(III); (2) in both cases there are large changes in cobalt–ligand bond lengths (Table V); (3) the complexes are about the same size and ammonia and water are closely related molecules. The similarities in the last of these properties give rise to very large intrinsic Franck–Condon barriers to electron exchange for both complexes (Table V). In fact, the Franck–Condon barrier alone would result in a self-exchange rate constant of ~10⁻⁶ M⁻¹ s⁻¹ for the Co(OH₂)₆³⁺,²⁺ couple. It seems very likely that much of the remaining factor of ~10⁷ in the inferred self-exchange rate constant is attributable to the small value expected for the two-center exchange integral in a σ*–σ* exchanging system in which the donor–acceptor overlap is com-

plicated by spin orthogonality.[4d] Thus, the intercept in Figure 1 yields a Co(OH₂)₆³⁺,²⁺ self-exchange parameter $\Delta G_{bb}^{\ddagger}$, which is similar in kind to the self-exchange rate constant for Co(NH₃)₆³⁺,²⁺. $\Delta G_{bb}^{\ddagger}$ is very large; about 75% of the numerical value of $\Delta G_{bb}^{\ddagger}$ originates in the Franck–Condon factor. There is a substantial contribution (~25%) of purely electronic terms to the observed value of $\Delta G_{bb}^{\ddagger}$. The self-exchange parameter obtained from the intercept of the correlation based on eq 2 should be regarded as a lower limit of the outer-sphere electron exchange between (¹A₁g)Co(OH₂)₆³⁺ and (⁴T₁g)Co(OH₂)₆²⁺. The electron-exchange integral would be larger for the Co(OH₂)₆³⁺,²⁺ self-exchange reaction than for the cross reactions, and this could lead to smaller values of κ_{el} in the latter. Different contributions of interactions with the solvent[45c] in the self-exchange and cross sections may also be a factor.

In view of the inferred contribution of purely electronic factors to $\Delta G_{bb}^{\ddagger}$, it is of interest that two reductants used in Figure 1 are high-spin Co(II) complexes: Co([15]aneN₄)(OH₂)₂²⁺ and Co(sep)²⁺. The Co(OH₂)₆³⁺/Co([15]aneN₄)(OH₂)₂²⁺ reaction fits the correlation very well ($\Delta G_{ab}^{\ddagger}$(calcd) = 53 kJ mol⁻¹, $\Delta G_{ab}^{\ddagger}$(obsd) = 49 kJ mol⁻¹), and the Co(OH₂)₆³⁺/Co(sep)²⁺ reaction fits reasonably well ($\Delta G_{ab}^{\ddagger}$(calcd) = 38 kJ mol⁻¹, $\Delta G_{ab}^{\ddagger}$(obsd) = 47 kJ mol⁻¹). These observations demonstrate that changes in spin multiplicity alone do not dictate the observed variations in reactivity. On the basis of a linear partitioning of contributions to the electronic term (e.g., leading to $(K_{el})_{ab} \approx (K_{el})_{aa}^{1/2}(K_{el})_{bb}^{1/2}$), we would estimate that the "spin only" contributions cannot reduce κ_{el} by a factor of more than 10³ for Co(sep)³⁺,²⁺ and spin only contributions are not important for Co([15]aneN₄)(OH₂)₂³⁺,²⁺. Since the contributions of spin multiplicity changes to the electronic term depend on the details of mixing of low-energy excited states,[4d] a considerable variation in spin multiplicity effects is to be expected.

There is a point of detail in the Co(OH₂)₆³⁺ reactions which deserves note. We have found that the *slopes* of free energy correlations (eq 2) are most nearly unitary for when the Franck-Condon only value of $\Delta G_{bb}^{\ddagger}$(Co) ≃ 100 kJ mol⁻¹ is used in the denominator of the quadratic term. This value has been used in obtaining the correlation in Figure 1. Values of the intercept are not significantly affected by this choice. This detail is important for internal consistency since only the Franck–Condon component of $\Delta G_{ii}^{\ddagger}$ should couple with the free energy dependence of the reaction.[3-5] In principle one might consider $\Delta G_{bb}^{\ddagger}$(Co) values of 100 kJ mol⁻¹ (based on the sum of Franck–Condon contributions, see Table V), 58 kJ mol⁻¹ (based on the experimental self-exchange rate constant[14]), or 132 kJ mol⁻¹ (based on the intercept in Figure 1). The slopes and intercepts obtained from a least-squares fit of the data points with these values of $\Delta G_{bb}^{\ddagger}$(Co) are respectively −1.00 ± 0.06 and 66 ± 3, −1.11 ± 0.10 and 67 ± 4, and −0.89

± 0.06 and 63 ± 3 kJ mol⁻¹. Since the theoretical slope is −1.00, somewhat better agreement is obtained from the calculated Franck–Condon components. The quadratic term is notoriously insensitive to precise values of the self-exchange rate constants, and the variations we have observed were found only because the range of $\Delta G_{ab}°$ spanned is very large. Nevertheless, it is important to ascertain that consistent values of the quadratic terms are used (i.e., Franck–Condon factors only) in drawing inferences about reactions claimed to be "nonabiabatic".

B. Possible Origins of the "Intercept Problem" in Co-$(OH_2)_6{}^{3+}$ Reactions. The huge discrepancy between the value of $\Delta G_{bb}{}^{*}(Co) = 132$ kJ mol⁻¹ inferred from the intercept in Figure 1 and value of $\Delta G_i{}^{*}(Co) = 58$ kJ mol⁻¹ determined for the $Co(CH_2)_6{}^{3+,2+}$ self-exchange reaction might in principle occur owing to (1) the intervention of an electronic excited state or (2) a difference in mechanism of the self-exchange and cross reaction. Before entering into a discussion of these two possible origins of the "intercept problem", it is important to note that the intercepts in Figure 1 do depend on the choice of Co(III)–Co(II) potential. A 0.1-V change in the potential only changes the intercept by ∼5 kJ mol⁻¹ and $\Delta G_{exch}{}^{*}$ by ∼10 kJ mol⁻¹. Differences in work terms may also contribute to the "intercept problem".

1. Possible Roles of Electronic Excited States. One may distinguish two ways in which electronic excited states may affect the observed electron-transfer rates: (a) by providing an accessible reaction channel with a relatively small activation barrier; (b) by providing a low-barrier reaction channel, but with the rate for population of the low-energy excited state comparable in magnitude to the net electron-transfer rate. The first of these possibilities should affect the self-exchange and cross reactions in comparable ways since such a reaction channel allowed for the self-exchange must also be allowed for the cross reactions (e.g., note that spin restriction could be relaxed for such an excited-state reaction channel). On the other hand, a kinetic competition between intramolecular population of excited states and intermolecular electron transfer could in principle account for the differences in intrinsic parameters inferred for self-exchange and cross reactions since the self-exchange reactions had reaction lifetimes >> 1 min while nearly all the cross-reaction lifetimes are less than 1 s.

The $Co^{II}L_6$ complexes considered in this report have a $^4T_{1g}$ ground state, and the spectroscopic energy gap to the lowest state in $Co(OH_2)_6{}^{2+}$ is $E(^2E) - E(^4T_{1g}) \simeq 52$ kJ mol⁻¹.[34] The thermal energy gap, $\Delta E°,° = E(^2E_g°) - E(^4T_{1g}°)$, will be appreciably smaller; we would put $\Delta E°,° \simeq 20$ kJ mol⁻¹. However, this state will be Jahn–Teller distorted, so one expects a very large Franck–Condon barrier to the $(^2E)Co-(OH_2)_6{}^{2+}/(^1A_{1g})Co(OH_2)_6{}^{3+}$ self-exchange (e.g., this is reasonably modeled by the low-spin $Co(N_4)(OH_2)_2{}^{3+,2+}$ self-exchange reactions of macrocyclic complexes[12g]). The combination of this barrier and the small populations of the excited state ($K \approx 10^{-4}$) would lead to $k_{exch} < 10^{-4}$ M⁻¹ s⁻¹, far smaller than the experimental value.[14]
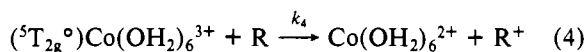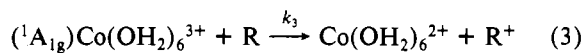
Simple ligand field arguments would predict $\Delta E°,° = E(^5T_{2g}°) - E(^1A_{1g}°)$ to be ∼120 kJ mol⁻¹ smaller for Co-$(OH_2)_6{}^{3+}$ than for $Co(NH_3)_6{}^{3+}$.[34] Wilson and Solomon[35] have recently found $\Delta E°,° \approx 102 \pm 28$ kJ mol⁻¹ for $Co(NH_3)_6{}^{3+}$, and Winkler, et al.[36] have used this value to estimate $\Delta E°,°$ ≃ 17.6 ± 28 kJ mol⁻¹ for $Co(OH_2)_6{}^{3+}$. Since $(^5T_{2g}°)Co-(OH_2)_6{}^{3+}$ appears to be nearly octahedral with about 12 pm

longer $Co-OH_2$ bonds than found in $(^1A_{1g})Co(OH_2)_6{}^{3+}$, one would expect a relatively small Franck–Condon barrier to the $(^5T_{2g}°)/Co(OH_2)_6{}^{2+}$ electron transfer.

The rate of spin relaxation in iron(III) complexes near spin equilibrium is on the order of 10^7 s⁻¹.[37] The bond length changes in these iron complexes are comparable to the changes in Co–OH₂ bond length in the process

$$(^1A_{1g})Co(OH_2)_6{}^{3+} \xrightarrow{k^*} (^5T_{2g}°)Co(OH_2)_6{}^{3+}$$

With use of the estimated $^1A_{1g} \rightarrow ^5T_{2g}°$ energy[35,36] and in comparison to spin relaxation in the iron complexes, a plausible estimate is $k^* \approx 10^5$ s⁻¹.[39,40] This is rapid enough that the $(^1A_{1g}) \rightleftharpoons (^5T_{2g}°)$ spin equilibrium would be established on the reaction time scales for all the reactions considered here. Consequently, the ratio k_3/k_4 would be expected to depend only on the value of $\Delta' E°,°$ and the ratio of Franck–Condon factors for (3) and (4), independent of the kind of reaction

$$(^1A_{1g})Co(OH_2)_6{}^{3+} + R \xrightarrow{k_3} Co(OH_2)_6{}^{2+} + R^+ \quad (3)$$

$$(^5T_{2g}°)Co(OH_2)_6{}^{3+} + R \xrightarrow{k_4} Co(OH_2)_6{}^{2+} + R^+ \quad (4)$$

investigated. This is the situation A noted above. Use of the estimated values of $\Delta' E°,°$, vibrational frequencies, and bond lengths[35,36,38,41] leads to $k_4 \approx 10^{-4}$ M⁻¹ s⁻¹ for the $Co(OH_2)_6{}^{3+,2+}$ self-exchange utilizing the excited-state pathway. Such a value is too small to account for the observed self-exchange and too large to be relevant to the cross reactions. As noted, this mechanism requires the same reaction channels for both classes of reaction.

While the parameters used in the above estimates are subject to considerable uncertainty, the theoretical treatment of spin-relaxation processes[40] suggests that the bond lengths in $(^5T_{2g}°)Co(OH_2)_6{}^{3+}$ would have to approach those of Co-$(OH_2)_6{}^{2+}$ in order for the value of k^* to be small enough (i.e., $k^* < 0.1$ s⁻¹) to allow the rate of excited-state population to discriminate between the cross- and self-exchange reactions of $Co(OH_2)_6{}^{3+}$. This does not seem very likely, and consequently, *an excited-state pathway is not likely to account for the "intercept problem"*. Nevertheless, it does seem surprising that excited-state reaction channels with small activation barriers do not contribute to the *outer*-sphere cross reactions. It may be that errors in current estimates of excited-state parameters, or some quirk of theory, do indeed permit very small values of k^*. It seems more likely that the correct value of $\Delta' E°,°$ is slightly larger than the current estimate, but still within error limits based on the Wilson and Solomon reference,[35] and that this pathway is not observed in any of the

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(34) Lever, A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: New York, 1968; p 183.

(35) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(36) Winkler, J. R.; Rice, S. F.; Gray, H. B. *Comments Inorg. Chem.* **1981**, *1*, 47.

(37) Dose, E. V.; Hoselton, M. A.; Sutin, N., Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1141.

(38) Friedman, H. L.; Hunt, J. P.; Plane, R. A.; Taube, H. *J. Am. Chem. Soc.* **1951**, *73*, 4028.

(39) Actually the rate of spin relaxation in Co(III) is expected to be intrinsically faster than spin relaxation in Fe(III)[40] so this estimate of k^* is probably a reasonable estimate of a lower limit based on structural information currently available. From ref 40 $k^* = (2\pi/h)g_i|V|^2G$, where $G = (1/h\omega)\{\exp[-S \coth X - px]|I_p(S/\sin hx), S = m\omega(\Delta r)^2/2h, x = h\omega/2k_BT, p = \Delta'E°,°/h\omega$, and I_p is a *p*th order Bessel function. On the basis of estimated structural parameters ($\omega_{alg}(^1A_{1g}) = 500$ cm⁻¹, $\omega_{alg}-(^5T_{2g}°) = 440$ cm⁻¹, $\Delta r = 12$ pm, and $\Delta'E°,° \approx 18$ kJ mol⁻¹), $p \simeq 3$, $S \approx 15$, and $h\omega/k_BT \approx 2.5$. Even with the small value of (V) ∼380 cm⁻¹ estimated in ref 40, Figure 2 in that reference implies that for isoenergetic spin relaxation, $k°(\Delta'E°,° = 0) \approx 10^{10}$ s⁻¹. On the basis of this estimate k^* ($\Delta'E°,° \approx 18$ kJ mol⁻¹) ∼ 10^7 s⁻¹.

(40) Buhks, E.; Navon, G.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 2918.

(41) Estimated with a classical harmonic oscillator model with bond length changes of 12 pm and force constants of 265 and 205 N pm⁻¹ respectively for $^1A_{1g}°$ and $^5T_{2g}°$; values based on a comparison with Co-$(NH_3)_6{}^{3+}$ and the corresponding reported[35] values. A small value (∼10 kJ mol⁻¹) is included for the expansion of the solvation volume as a consequence of the excitation. See: Endicott, J. F.; Heeg, M. J.; Gaswick, D. C.; Pyke, S. C. *J. Phys. Chem.* **1981**, *85*, 1777.

reactions owing to a combination of the prohibitive promotion energy and the necessary Franck–Condon factors.

2. Concerning the Possibility of a Water-Bridged, Inner-Sphere Pathway. The most obvious way in which the measured self-exchange rate could be so many orders of magnitude larger than the self-exchange rate inferred from cross reactions is if the former reaction is inner sphere while the cross reactions are outer-sphere in mechanism.[42] However, the rate law requires an acid-independent pathway, and the bridging ligand would appear to be a water molecule.

Since the inner-sphere reaction coordinate involves metal–ligand homolysis, the activation barrier associated with this pathway involves contributions from the metal–bridging-ligand homolytic bond dissociation energy[43] as well as the perhaps more obvious steric (r_e in ref 43), transition-state bonding (δ in ref 43), and Franck–Condon (contained in ν_e in ref 43) factors. Thus, for cobalt complexes, the activation barrier to an inner-sphere process is reduced compared to the outer-sphere pathway when (a) the homolysis bond energy is relatively small, (b) the bridging ligand can mediate $\sigma^*-\sigma^*$, donor–acceptor overlap (thereby reducing that part of $\Delta G_{ii}^{\ddagger}(Co)$ which originates from electronic terms),[12h] and (c) this multicentered bonding interaction can reduce the Franck–Condon barrier (compared to the harmonic oscillator limit).[43]

Recent work[44] has found a threshold energy of ~ 300 kJ mol^{-1} for photohomolysis of $Co(N_4)(OH_2)_2^{3+}$ (N_4 = $Me_4[14]$tetraeneN$_4$).

$$Co(N_4)(OH_2)_2^{3+} + h\nu \rightarrow Co(N_4)(OH_2)^{2+} + \cdot OH_2^{+}$$
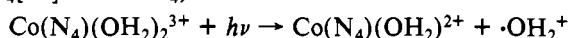
Since $Co(OH_2)_6^{3+}$ is about 1.3 V more oxidizing than for the macrocyclic cobalt(III) complex, the homolysis threshold in the hexaaquo complex is probably of the order of 230 kJ mol^{-1}.[45,46] This is comparable to the Co–X bond dissociation energies (~ 200 kJ mol^{-1}) in $Co(N_4)(OH_2)X^{2+}$ complexes (X = Cl, CH_3) for which X has been shown to be an effective bridging ligand.[43] From the point of view of energetics this could be an accessible reaction pathway for the $Co(OH_2)_6^{3+,2+}$ couple. On the other hand putting H_2O^+ into a three-center bonding configuration might be accomplished only with some energy expenditure, and if so, this would reduce its effectiveness as a bridging ligand. In this regard it is interesting to note that the measured $Co(OH_2)_6^{3+,2+}$ self-exchange rate falls between the self-exchange rates for Cl- and CH_3-bridged $Co(N_4)(OH_2)X^{2+}/Co(N_4)(OH_2)_2^{2+}$ reactions.[12h,43,47–49]

The limited available information concerning activation parameters is consistent with a smaller Franck–Condon barrier to the observed $Co(OH_2)_6^{3+,2+}$ self-exchange reaction than is inferred from outer-sphere cross reactions. Thus, the $Co(OH_2)_6^{3+}/Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ reaction is strongly temperature dependent: $\Delta H_{ab}^{\ddagger} = 50 \pm 2$ kJ mol^{-1}. This is related to the activation enthalpies of the respective exchange reactions by[51] eq 5, where $\alpha = \Delta G_{ab}°/4(\Delta G_{aa}^{\ddagger} +$

$$\Delta H_{ab}^{\ddagger} = \left[\frac{\Delta H_{aa}^{\ddagger} + \Delta H_{bb}^{\ddagger}}{2} \right](1 - 4\alpha^2) + \Delta H_{ab}°(1 + 2\alpha)$$

$$(5)$$

$\Delta G_{bb}^{\ddagger} - w_{ab}$). For this reaction we obtain an intrinsic activation enthalpy,[52] $\Delta H_1^{\ddagger} \simeq 100 \pm 20$ kJ mol^{-1}. This may be compared to $^1/_2(\Delta H_{aa}^{\ddagger} + \Delta H_{bb}^{\ddagger}) \simeq {}^1/_2(\leq 50^{53} + 43^{14})$ kJ $mol^{-1} \leq 46$ kJ mol^{-1}. Franck–Condon factors estimated in Table IV would give $^1/_2(\Delta H_{aa}^{\ddagger} + \Delta H_{bb}^{\ddagger}) \simeq 70$ kJ mol^{-1} in somewhat better agreement with observation.

The contrast with the possibility of water bridging in other systems is also of interest. A reasonably small value for the metal–ligand homolysis bond dissociation energy is an important prerequisite for an effective bridging pathway. Owing to the instability of H_2O^+, a water-bridged electron-transfer pathway is only plausible for reactions involving a very strongly oxidizing metal such as in $Co(OH_2)_6^{3+}$. For example, based on the difference in redox potentials we would predict the water-bridged pathway to be $\sim 10^{10}$ times more important for the $Co(OH_2)_6^{3+}$ couple than for the $Fe(OH_2)_6^{3+,2+}$ couple.[54] From the point of view of simple energetics, it seems unlikely that a water-bridged pathway can be important for many redox couples; e.g., the Fe^{2+}, V^{2+}, and U^{3+} reductions of $Co(OH_2)_6^{3+}$ seem reasonably consistent with the other outer-sphere reactions considered in Figure 1. Large deviations from the correlation in Figure 1 would only be likely for reactions of $Co(OH_2)_6^{3+}$ with hard to oxidize metals (Mn^{II}, Ce^{III}, etc.) for which the inner-sphere self-exchange pathway offers significant

(42) An identical conclusion has been reached by Hush and was brought to our attention after our work was submitted for publication: Hush, N. S. *ACS Symp. Ser.*, in press.

(43) (a) Endicott, J. F.; Wong, C. L.; Ciskowski, J. M.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980**, *102*, 2100. (b) Endicott, J. F.; Balakrishnan, K. P.; Wong, C. L. *Ibid.* **1980**, *102*, 5519.

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(45) In this estimate we have made a 70 kJ mol^{-1} correction for entropic differences in the $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+,2+}$ and $Co(OH_2)_6^{3+}$ redox couples.[46]

(46) (a) Yee, E. L.; Cave, R. J.; Gayer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131. (b) Weaver, M. J., private communication, 1979. (c) Weaver, M. J.; Yee, E. L. *Inorg. Chem.* **1980**, *19*, 1936.

(47) A reviewer has called our attention to some of the "problems" with the concept of a water-bridged pathway. The actual meaning of a "water"-bridged transition state may be a little obscure since proton exchange with the medium is expected to be rapid. It is conceivable that at the time of electron transfer, the bridging ligand may "look" more like OH^- than H_2O. In order for a very rapid transfer of a proton from a $[(H_2O)_5Co]_2OH_2^{5+}$ species to *solvent water* (a requirement of the rate law) to be kinetically significant, it would have to occur completely during the reactant collision lifetime ($< 10^{-11}$ s); i. e., pK_a would have to be less than -3 for the water-bridged species. It seems more likely that there is some stretching of the O–H bond in concert with approach of the $Co(OH_2)_5^{2+}$ reactant partner. The apparently slower $Co(OD_2)_6^{3+,2+}$ than $Co(OH_2)_6^{3+,2+}$ self-exchange[48] is consistent with partial proton transfer to solvent.[49] This isotope effect is also in the direction expected for vibrational activation of electron transfer or for intersystem crossing.[50]

(48) Shankar, J.; DeSouza, B. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 187.

(49) With the assumption, of course, that the rates of H^+ transfer to H_2O and D^+ transfer to D_2O follow the pattern observed for $H^+ + OH^-$ and $D^+ + OD^-$ (Eigen, M.; Kruse, W.; Maass, G.; deMaeyer, L. *Prog. React. Kinetics* **1964**, *2*, 287.

(50) Buhks, E.; Bixon, M.; Jortner, J. *J. Phys. Chem.* **1981**, *85*, 3763.

(51) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

(52) Values of parameters used are $\Delta G_{ab}° = 131$ kJ mol^{-1} (see Table IV), $\Delta G_{aa}^{\ddagger} = 70$ kJ mol^{-1},[12] $\Delta G_{bb}^{\ddagger} = 58.1$ kJ mol^{-1},[14] $w_{ab} = 7.2$ kJ mol^{-1}, $\Delta S_{ab}° = 83$ kJ mol^{-1},[46] $\Delta H_{ab}° = -106$ kJ mol^{-1}, and $\alpha = -0.269$.

(53) For the $Co(Me_2[14]4,7-dieneN_4-6-one)(OH_2)_2^{3+}/Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ reaction, $\Delta H^{\ddagger} \simeq 50$ kJ mol^{-1}.[12g] The reorganizational energy of $Co(Me_4[14]tetraaene-N_4)(OH_2)_2^{3+,2+}$ is smaller than that of $Co(Me_2[14]4,7-dieneN_4-6-one)(OH_2)_2^{3+,2+}$.[12g]

(54) This is an overestimate if the

$$Fe - \overset{\overset{\displaystyle H}{|}}{O} - Fe$$
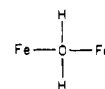
is significantly stronger than the

$$Co - \overset{\overset{\displaystyle H}{|}}{O} - Co$$
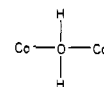
bond, or if the $Fe^{III}-OH_2$ homolysis bond dissociation energy is significantly smaller than the $Co^{III}-OH_2$ bond energy. The *differences* in these bond energies would have to be ~ 50 kJ mol^{-1} to bring the inner-sphere pathway into the 5 m^{-1} s^{-1} range. In making this estimate we have used $\Delta E° = 1.13$ V and LFSE ≈ 60 kJ mol^{-1} for $Co(OH_2)_6^{3+}$. See: Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 494. The fair agreement of the Co^{3+}/Fe^{2+} reaction with the correlation in Figure 1 is consistent with a very large ratio of the rates of inner-sphere reactions of these complexes since the cross reaction apparently finds no advantages in the inner-sphere pathway.

advantage over the outer-sphere pathway.

Conclusions

This study has demonstrated the following: (1) For all reactions for which the critical parameters are known, outer-sphere reductions of $Co(OH_2)_6^{3+}$ exhibit a classical Marcus dependence on the reaction free energy change.

(2) The $Co(OH_2)_6^{3+,2+}$ self-exchange parameter required to correlate these outer-sphere cross reactions is ~ 12 orders of magnitude smaller than the experimental value found for the $Co(OH_2)_6^{3+,2+}$ self-exchange.

(3) The calculated Franck–Condon factors imply a self-exchange rate ~ 7 orders of magnitude smaller than the experimental value found for $Co(OH_2)_6^{3+,2+}$.

(4) The outer-sphere cross reactions of $Co(OH_2)_6^{3+}$ and the $Co(OH_2)_6^{3+,2+}$ self-exchange reactions differ in mechanism,

with the latter most likely proceeding through a "water-bridged" pathway.

(5) Franck–Condon factors alone do not account for the outer-sphere behavior of the $Co(OH_2)_6^{3+,2+}$ couple; a significant contribution of electronic terms is likely.

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Exchange Interaction in Multinuclear Transition-Metal Complexes. 2.[1] Synthesis and Structural and Magnetic Studies of a Dinuclear Iron(III) Derivative of the Heptadentate Schiff Base Trisalicylidenetriethylenetetramine

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In an attempt to experimentally determine magnetostructural relationships for magnetically condensed iron(III) dinuclear systems, we have synthesized the compound $Fe_2L(OCH_3)Cl_2$ (L^{3-} is the heptadentate trianion of the Schiff base trisalicylidenetriethylenetetramine) and investigated its X-ray structure as well as its temperature dependence on magnetic susceptibility. $Fe_2L(OCH_3)Cl_2$ crystallizes in the tetragonal space group $P4_2/n$. The structure consists of dinuclear units. The two iron atoms are asymmetrically bridged by a phenolic oxygen and a methoxy group. The metal coordination geometry is distorted octahedral, the six coordination sites being occupied by two cis oxygens and two cis nitrogens of L^{3-}, a terminal chlorine atom, and a bridging methoxy group. The magnetic susceptibility of powdered samples of the compound has been examined in the temperature range 5–290 K. The best fit to the Van Vleck equation yielded $J = -8.0$ cm^{-1}.

Introduction

The correlation between the structural and magnetic properties of dinuclear copper(II) and chromium(III) compounds involving four-membered M–O–M–O rings is becoming increasingly well documented. It has been found for these systems that the magnitude and sign of the exchange coupling, as reflected by the interaction constant, J, are principally determined by the geometry of the bridging unit,[2,3] the electron density at the oxygen bridge,[4,5] and in the case of copper(II), distortions from planar ligand environments at the metal center.[6] Molecular orbital[7] and angular overlap[8] approaches have been used to discuss magnetostructural relationships in copper(II) dimers.

How the exchange interaction in iron(III) systems of the aforementioned type is affected by structural changes remains to be established.[1,9] In the previous paper[1] we have supplemented the few iron(III) systems[9,10] for which both structural and magnetic properties have been examined with the first example of a completely characterized dimethoxo-bridged complex, this being di-μ-methoxy-dichloro[1,4-piperazine-bis(N-ethylenesalicylaldiminato)]diiron(III), Fe_2L'-$(OCH_3)_2Cl_2$. Here we report the synthesis and X-ray structural and magnetic characterization of a derivative of the closely related ligand trisalicylidenetriethylenetetramine (called LH_3 hereafter), $Fe_2L(OCH_3)Cl_2$, containing a Fe–OMe–Fe–OPh bridging unit.

Experimental Section

Measurements. There were performed as described previously.[1]

Syntheses. LH_3. This ligand has been prepared according to known procedures.[11]

$Fe_2L(OCH_3)Cl_2$. A 15-mL quantity of a 0.1 M solution of CH_3ONa in methanol was added to a solution of $FeCl_3 \cdot 6H_2O$ in the same solvent (0.54 g, 2 mmol, in 15 mL). To the resulting solution, heated at 70 °C, was added with stirring LH_3 dissolved in methanol (0.46 g, 1 mmol). The reaction mixture was kept at 70 °C for 15 min and then allowed to cool to ~ 15 °C. Crystallization was allowed to continue for ~ 24 h before brown prismatic crystals were collected by filtration,

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