conditions suggests a cage fluxional process that need not be very dependent on the nature and number of substituents. By comparison, intramolecular substituent migration rates could well be expected to be considerably dependent on (a) some fraction of the B–X bond strengths (an expected ~55 kJ/mol difference for B–Cl vs. B–C),[22] (b) the number of such bonds (if the migration for polysubstituted compounds is concerted), and (c) steric influences in some instances (e.g., the tetramethyl derivative). Nevertheless, intramolecular substituent migration, although considered unlikely, cannot be entirely ruled out; but this problem probably cannot be settled until a $C_2B_5H_7$ molecule that is isotopically enriched at specific sites becomes a synthetic reality.

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Registry No. 5-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-32-4; 3-CH_3-*closo*-2,4-$C_2B_5H_6$, 23940-13-8; 1-CH_3-*closo*-2,4-$C_2B_5H_6$, 23810-31-3; *closo*-2,4-$C_2B_5H_7$, 20693-69-0.

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Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48824

Reduction Kinetics of Pentaamminecobalt(III) Complexes Containing 4,4′-Bipyridine and Related Ligands at Mercury, Platinum, and Gold Electrodes

VISWANATHAN SRINIVASAN, STEPHEN W. BARR, and MICHAEL J. WEAVER*

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The electroreduction kinetics of pentamminecobalt(III) complexes containing 4,4′-bipyridine (BP), 1,2-bis(4-pyridyl)ethane, *trans*-1,2-bis(4-pyridyl)ethylene, pyridine, or pyrazine ligands were studied at mercury–, platinum–, and gold–aqueous interfaces in order to explore the ability of such nitrogen heterocycles to mediate electron transfer at metal surfaces. These reactivity patterns are compared with those for corresponding homogeneous reactions; the electrochemical reduction rates of the nitrogen-heterocycle-containing complexes were found to be considerably faster than expected from their outer-sphere homogeneous reactivities relative to the rates of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_6^{3+}$ reduction. Likely causes of the apparent mediation of the heterogeneous reactions by the heterocyclic ligands are discussed. The primary factor appears to be the ability of these ligands to induce the adsorption of Co(III), as measured for $Co(NH_3)_5py^{3+}$ and $Co(NH_3)_5BP^{3+}$ at mercury electrodes by using chronocoulometry.

Introduction

We have recently been examining the electrochemical kinetics of various transition-metal complexes that engage in one-electron outer- and inner-sphere reactions at metal surfaces.[1-4] One aim of this work is to explore in a systematic manner the similarities and differences between the energetics of such simple redox reactions at metal electrodes and in homogeneous solution.[2,3,5,6,8,9] Our initial studies at the well-defined mercury–aqueous interface[1-4] have more recently been broadened to include a number of solid metals, particularly platinum, gold, and silver.[5,7] Methods have been developed for distinguishing between outer-sphere and some inner-sphere (ligand-bridged) reaction mechanisms at both mercury[1,10] and solid metal surfaces.[5] Large reactivity variations for some outer-sphere as well as anion-bridged pathways have been observed as the electrode material is altered,[5,7] illustrating the important influences that the electrode surface structure can exert upon the reaction energetics.

Although somewhat neglected by electrochemists, the reduction of pentaamminecobalt(III) complexes provides a valuable reactant class with which to explore structural factors in electrochemical kinetics, especially in view of the wealth of homogeneous kinetic information that has become available for such systems containing a wide variety of bridging ligands. We have found that the effect of systematic variations in the double-layer structure upon the outer-sphere reduction kinetics of $Co(NH_3)_5X$ complexes ($X = NH_3$, OH_2, F^-, OH^-) is uniformly in reasonable agreement with the predictions of the simple Gouy–Chapman–Stern–Frumkin (GCSF) model, both at mercury[2,11] and at solid electrodes.[5,7] Complexes containing adsorbing anionic ligands ($X = Cl^-$, Br^-, NCS^-, NO_3^-, etc.) are usually reduced via more facile ligand-bridged pathways,[2,5]

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Table I. Electrochemical Rate Parameters for the Reduction of Various $Co^{III}(NH_3)_5X$ Complexes at Mercury, Platinum, and Gold Electrodes in Perchlorate Electrolytes

	k_{app}, cm s^{-1} (at 0 mV vs. SCE)					α_{app}		
complex[a]	$Hg^{b,e}$	$Pt^{c,e}$	$Au^{c,e}$	Pt $(1^-)^{c-e}$	Au $(I^-)^{c-e}$	$Hg^{b,e}$	$Pt^{c,e}$	$Au^{c,e}$
$R-OH_2^{3+}$	5.0×10^{-4}	7.8×10^{-4}	6.7×10^{-3}	1.8×10^{-2}	7.0×10^{-2}	0.55	0.53	0.65
$R-NH_3^{3+}$	3×10^{-7}	4.3×10^{-5}	1.7×10^{-4}	8.4×10^{-5}	3.3×10^{-4}	0.80	0.56	0.82
$R-Me_2SO^{3+}$	1.6×10^{-3}	8.4×10^{-4}	1.1×10^{-2}	6.0×10^{-2}	0.16	0.63	0.56	0.58
$R-py^{3+}$	1.9×10^{-3}	2.2×10^{-2}	2.7×10^{-2}	1.9×10^{-2}	3.6×10^{-2}	0.81	0.71	0.73
$R-pyz^{3+}$	5.0×10^{-3}	2.6×10^{-3}	9.2×10^{-2}	0.11	0.81	0.66	0.51	0.57
$R-BP^{3+}$	~0.3	~0.5	~1.9	~0.5	~1.3	0.95	0.67	0.66
$R-BPH^{4+}$	1.9×10^{-2}	1.7×10^{-2}	4.2×10^{-2}	4.3×10^{-3}	1.4×10^{-2}	0.85	0.60	0.66
$R-BPAH^{4+}$	7.5×10^{-3}	5.2×10^{-3}	6.5×10^{-3}	6.5×10^{-3}	9.2×10^{-4}	0.75	0.61	0.67
$R-BPEH^{4+}$	8.2×10^{-2}	2.4×10^{-2}	2.2×10^{-2}	2.4×10^{-2}	3.7×10^{-2}	0.9	0.61	0.62

[a] R = $Co^{III}(NH_3)_5$; Me_2SO = dimethyl sulfoxide; py = pyridine; pyz = pyrazine; BP = 4,4′-bipyridine; BPA = 1,2-bis(4-pyridyl)ethane; BPE = *trans*-1,2-bis(4-pyridyl)ethylene. BPH, BPAH, and BPEH refer to the corresponding monoprotonated ligands. [b] Determined in 0.5 M $LiClO_4$ containing 1 mM $HClO_4$, unless otherwise noted. [c] Determined in 0.1 M $NaClO_4$ containing 1 mM $HClO_4$, unless otherwise noted. [d] Values of k_{app} after the addition of 5 mM NaI. [e] Values of k_{app} and α_{app} for reduction of $R-BP^{3+}$ and corresponding protonated species $R-BPH^{4+}$ determined from rate–pH dependence combined with pK_a for complex (see text).

especially at noble metals where such complexes are tenaciously adsorbed.[5] By a combination of corresponding kinetics and adsorption data for inner-sphere reactants, some of these reactivity patterns have been analyzed in terms of "thermodynamic" and "intrinsic" contributions to the electron-transfer barrier.[3,5]

It is of interest to extend these studies to $Co(NH_3)_5X$ complexes containing organic ligands, particularly those having functional groups capable of binding to the electrode, in order to explore the ability of organic structural units to mediate electron transfer at metal surfaces. One interesting class of ligands is provided by 4,4′-bipyridine and related nitrogen heterocycles in view of the observed ability of these species to act as bridging groups in homogeneous solution, including reactions involving pentamminecobalt(III).[12,13] The homogeneous reduction of these complexes has been thoroughly investigated by using a number of reducing agents that can induce outer- as well as inner-sphere reaction pathways.[12-18] In addition to the possibility of reactant adsorption occurring via π-orbital overlap between the aromatic rings and the electrode surface, complexes containing such ligands may bind to electrode surfaces via the exposed pyridyl nitrogen to yield entities similar to the binuclear complexes that can be formed with homogeneous reductants.[12,13]

In the present paper, the electroreduction kinetics of $Co^{III}(NH_3)_5X$ complexes with X = 4,4′-bipyridine, bis(4-pyridyl)ethane (BPA), bis(4-pyridyl)ethylene (BPE), pyrazine, and pyridine at the mercury–, platinum–, and gold–aqueous interfaces are reported and compared with corresponding homogeneous and electrochemical rate data for $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_6^{3+}$ reduction in order to assess the kinetic influence of the nitrogen heterocycle ligands. These latter two reactions were chosen for comparison since we have previously examined their electrode kinetics in detail at both mercury[2,6] and solid electrodes[5,7] and found them to exhibit the behavior expected for simple outer-sphere electrochemical pathways. The results demonstrate the particular effectiveness of nitrogen heterocyclic ligands in mediating electron transfer at metal surfaces.

Experimental Section

$[Co(NH_3)_5OH_2](ClO_4)_3$ was synthesized as in ref 19 and $[Co(NH_3)_6](ClO_4)_3$ as in ref 20. $[Co(NH_3)_5Me_2SO](ClO_4)_3$ (Me_2SO = dimethyl sulfoxide), prepared as in ref 21, was used as the starting point for the synthesis of $[Co(NH_3)_5py](ClO_4)_3$ (py = pyridine),[21] $[Co(NH_3)_5pyz](ClO_4)_3$ (pyz = pyrazine),[22] and $[Co(NH_3)_5BP](ClO_4)_3$ (BP = 4,4′-bipyridine).[23] $[Co(NH_3)_5BPA](ClO_4)_3$ (BPA = 1,2-bis(4-pyridyl)ethane) and $[Co(NH_3)_5BPE](ClO_4)_3$ (BPE = *trans*-1,2-bis(4-pyridyl)ethylene) were prepared from $[Co(NH_3)_5OH_2](ClO_4)_3$ as described in ref 12. The perchlorate salts were purified by precipitation upon the addition of a concentrated solution of sodium perchlorate. The BP, BPA, and BPE ligands (Aldrich) were twice recrystallized from water. Most inorganic salts were recrystallized from water prior to use.

The fabrication and surface pretreatment of the platinum and gold electrodes, and the apparatus and techniques employed for the electrochemical kinetic measurements, were essentially as described in ref 7. Electrochemical rate data at mercury electrodes were evaluated with dc or normal pulse polarography utilizing a dropping mercury electrode with a mechanically controlled drop time of 2 s. Most rate data at platinum and gold electrodes were obtained with rotating-disk voltammetry. Since no significant anodic back-reactions (Co(II) → Co(III)) can occur except at extremely positive electrode potentials,[2] the conventional data analyses for totally irreversible voltammetric and polarographic waves could be employed.[7] As before,[7] rate parameters at the solid surfaces typically decreased slowly with time following the immersion of a freshly pretreated electrode so that they were usually obtained within a few ($\lesssim$10) minutes after the electrode cleaning.

Adsorption data for $Co(NH_3)_5BP^{3+}$ and $Co(NH_3)_5py^{3+}$ were obtained at a dropping mercury electrode with use of single-step chronocoulometry. A microcomputer-based data acquistion and analysis system was utilized for these measurements, the charge–time transients of 10–20 ms duration being stored in digital form in real time with a data acquistion rate of 10 kHz. Potential steps were selected so that the final potential was as negative as possible in order to minimize the adsorption of the bipyridine or pyridine ligands set free upon reduction. Although 4,4′-bipyridine is reduced at around −600 mV vs. SCE in strongly acidic media, the use of weakly acidic electrolytes (pH ~3) allowed final potentials as negative as −1000 mV to be employed for $Co(NH_3)_5BP^{3+}$ as well as $Co(NH_3)_5py^{3+}$ reduction without significant complications from ligand reduction on the time scale of the potential step.

Electrode potentials are quoted with respect to the saturated calomel electrode (SCE). All kinetic and adsorption measurements were performed at 24.0 ± 0.5 °C.

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Table II. Effects of Altering Double-Layer Composition on Reduction Kinetics of $Co^{III}(NH_3)_5X$ Complexes at Mercury Electrodes at 0 mV vs. SCE

	0.4 M KPF_6			0.3 M KF		
complex[a]	k_{app},[b] cm s^{-1}	α_{app}[b]	$\Delta \log k_{app}$[d]	k_{app},[c] cm s^{-1}	α_{app}[c]	$\Delta \log k_{app}$[e]
R-OH_2^{3+}	$\sim 5 \times 10^{-6}$	0.72	−2.0	$\sim 5 \times 10^{-7}$	0.7	−3.0
R-py^{3+}	2.5×10^{-4}	0.95	−0.9	9×10^{-6}	0.92	−2.3
R-pyz^{3+}	2.0×10^{-4}	0.81	−1.4	3.5×10^{-6}	0.96	−3.2
R-BP^{3+}				6.5×10^{-4}	0.88	−2.7
R-BPA^{3+}				2.3×10^{-4}	0.88	
R-BPE^{3+}				1.0×10^{-3}	0.85	

[a] For nomenclature see footnote *a* to Table I. [b] Rate parameters determined in 0.4 M KPF_6 + 1 mM $HClO_4$ (pH ~3). [c] Rate parameters determined in 0.3 M KF + 1 mM HF (pH ~4.5). [d] Change in log k_{app} when substituting 0.5 M $LiClO_4$ by 0.4 M KPF_6. [e] Change in log k_{app} when substituting 0.5 M $LiClO_4$ by 0.3 M KF.

Results

Electrochemical rate–potential data for the reduction of eight cobalt(III) pentaammine complexes containing aquo, ammine, pyridine, 4,4′-bipyridine, and related ligands in perchlorate electrolyte at mercury, platinum, and gold electrodes are summarized in Table I as values of the apparent (measured) rate constant k_{app}[5] measured at 0 mV vs. SCE, along with the corresponding value of the apparent transfer coefficient α_{app} ($=-(RT/F)(\mathrm{d}\ln k_{app}/\mathrm{d}E)$). Since the Tafel plots (i.e., the ln k_{app} vs. E plots) for each system were found to be approximately linear within the range of values of k_{app} (ca. 10^{-4} to 5×10^{-2} cm s^{-1}) that were conveniently accessible with normal pulse polarography and rotating-disk voltammetry, one value of k_{app} and α_{app} suffices to describe completely the observed kinetic behavior for each system. The desirability of comparing electrochemical rate parameters for related systems at a common electrode potential is clear;[7] the value of 0 mV vs. SCE, albeit somewhat arbitrary, was selected since the extent of linear extrapolation of the Tafel plots that was necessary in some cases was thereby minimized.

The kinetic parameters at mercury electrodes given in Table I were obtained in acidified 0.5 M $LiClO_4$ while those at platinum and gold surfaces refer to acidified 0.1 M $NaClO_4$. The former electrolyte allowed the effects of varying the acidity to be studied quantitatively with use of constant ionic strength mixtures with $HClO_4$. The latter base electrolyte was employed with the solid electrodes since it could be obtained in an especially pure state; this is desirable on account of the sensitivity of such surfaces to contamination by solution impurities.[5,7] The kinetics of most reactions were found to be essentially independent of pH in the range pH 1–3 at all three surfaces. The single exception is $Co(NH_3)_5BP^{3+}$; the reduction rates of this complex were found to decrease at all three electrodes as the pH was lowered to ca. pH 2, whereupon the rates became pH independent.

This pH dependence is most likely due to protonation of the exposed nitrogen on the coordinated bipyridine ligand to form $Co(NH_3)_5BPH^{4+}$, which is reduced more slowly than the unprotonated form $Co(NH_3)_5BP^{3+}$. In order to check this possibility, we determined the pK_a for the equilibrium $Co(NH_3)_5BPH^{4+} \rightleftharpoons Co(NH_3)_5BP^{3+} + H^+$ by means of a pH titration, employing 1 mM $[Co(NH_3)_5BP](ClO_4)_3$ in 0.5 M $LiClO_4$, with perchloric acid as the titrant. A value of pK_a = 4.0 ± 0.2 was obtained ($\mu = 0.5$). This is close to pK_1 for the free ligand (~3.8) at the same ionic strength obtained by Debye–Hückel extrapolation of the published data[24] (μ = 0.05–0.2), where pK_1 refers to the loss of the first proton from the diprotonated ligand ($BPH_2^{2+} \rightleftharpoons BPH^+ + H^+$). Similar pH titrations performed for $Co(NH_3)_5BPA^{3+}$ and $Co(NH_3)_5BPE^{3+}$ indicated that for both complexes p$K_a \gtrsim 5.0$. These latter two complexes are therefore entirely protonated under most conditions employed for the electrode kinetics experiments (pH $\lesssim$3).[25] Assuming that the rate–pH dependence for $Co(NH_3)_5BP^{3+}$ reduction is, due to parallel reduction of the free complex and its protonated form, we combined the pK_a for $Co(NH_3)_5BP^{3+}$ with the kinetic data to yield separate values of k_{app} and α_{app} for the reduction of $CO(NH_3)_5BP^{3+}$ and $Co(NH_3)_5BPH^{4+}$ at mercury, platinum, and gold electrodes. These values are also listed in Table I.

The reduction kinetics for most complexes at mercury electrodes were also investigated in 0.4 M KPF_6 and 0.3 M KF supporting electrolytes in order to ascertain the rate response to variations in the double-layer composition. Thus PF_6^- and especially F^- anions are specifically adsorbed to a markedly smaller extent than ClO_4^- in the potential region (+100 to −200 mV) where the electrode kinetics were monitored.[26] Consequently, the average potential at the reaction plane ϕ_{rp} becomes less negative (and eventually positive) as perchlorate is replaced by hexafluorophosphate or fluoride electrolytes to an extent that will depend on the position of the reaction site relative to the outer Helmholtz plane (OHP).[26] Provided that the reactant can be treated as a point charge, the variation in ϕ_{rp}, $\Delta\phi_{rp}$, brought about by alterations in the double-layer structure will yield variations in k_{app}, $\Delta \log k_{app}$, at a given electrode potential E according to

$$(\Delta \log k_{app})_E = f(\alpha_{cor} - Z)(\Delta\phi_{rp})_E \qquad (1)$$

where Z is the charge number of the reactant, α_{cor} is the work-corrected transfer coefficient (~0.5), and $f = F/RT$.[1,2] Spherical, or nearly spherical, reactants such as $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_6^{3+}$ are found to yield values of $\Delta\phi_{rp}$ from eq 1 that are in accordance with the expectations of simple double-layer models.[2] However, it might be expected that unsymmetrical complexes such as the heterocycle-containing reactants would behave substantially differently, especially if the complex is strongly oriented by the double-layer field. Table II summarizes such values of $\Delta \log k_{app}$, as well as k_{app} and α_{app}, at 0 mV vs. SCE for the reduction of the various cobalt(III) pentaammine complexes at mercury electrodes resulting from the substitution of 0.5 M $LiClO_4$ by 0.4 M KPF_6 (pH 3.0) and 0.3 M KF (pH 4.5) electrolytes. It is seen that the values of k_{app} for each complex are decidedly smaller in KPF_6 and especially KF electrolytes so that large and negative values of $\Delta \log k_{app}$ are uniformly obtained, as expected on the basis of eq 1 given that $Z = 3$ for all these reactants.

Such measurements are less feasible at platinum and gold electrodes since the kinetic data are inherently less reproducible

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(25) Given that the pK_1 for $BPEH_2^+$ is estimated to equal ca. 5.0 at $\mu = 0.5$ (from D. K. Lavallee and E. B. Fleischer, *J. Am. Chem. Soc.*, **94**, 2583 (1972)), a value of the pK_a for $Co(NH_3)_5BPEH^{4+}$ for ca. 5 would be expected given the similarity of pK_a for $Co(NH_3)_5BPH^{4+}$ and BPH_2^{2+}. This latter result suggests that the interaction between the Co(III) and H^+ at the opposite ends of the 4,4′-bipyridine ligands in $Co(NH_3)_5BPH^{4+}$ is weak, at least at high ionic strengths.

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and little information is available regarding the extent of anion adsorption. Nevertheless, one way of modifying the double-layer composition of these surfaces that has yielded useful mechanistic information involves monitoring the rate response resulting from the addition of small quantities (a few millimolar) of iodide ions.[5] Iodide anions are tenaciously adsorbed at platinum and gold under these conditions;[27] they have been found to effectively eliminate inner-sphere pathways for the reduction of some cationic cobalt(III) pentaammine complexes containing potential bridging anions, presumably by denying the anion access to the metal surface.[5] Thus substantial (up to 10^5-fold) rate decreases have been found for such reactions at platinum and gold electrodes upon iodide addition, instead of the rate increases predicted from eq 1. In contrast, rate responses in accordance with eq 1 have been observed under these circumstances for structurally similar cationic reactants that reduce via outer-sphere mechanisms. These experiments can therefore provide a diagnostic criterion of reaction mechanism.[5] Table I includes values of k_{app} at 0 mV vs. SCE obtained for each reactant at platinum and gold electrodes in 0.1 M $NaClO_4$ (pH 3), both before and after the addition of 5 mM NaI. It is seen that only mild rate responses were obtained for most complexes, although smaller rate increases were typically observed for the heterocycle-containing complexes in comparison with those for $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5OH_2^{3+}$ reduction, and significant rate decreases were obtained for some reactants.

Single-step chronocoulometric measurements of reactant adsorption in 0.5 M $LiClO_4$ (pH 2.5–3) for mercury electrodes at an initial potential of +200 mV vs. SCE failed to detect adsorption of $Co(NH_3)_5OH_2^{3+}$, as expected. However, $Co(NH_3)_5BPH^{4+}$ and $Co(NH_3)_5py^{3+}$ were found to be detectably adsorbed under these conditions. Thus, for $Co(NH_3)_5BPH^{4+}$, $\Gamma = 5 \times 10^{-11}$ mol cm^{-2} for bulk concentration, $C^b = 1$ mM, and for $Co(NH_3)_5py^{2+}$, $\Gamma = 2.0 \times 10^{-10}$ mol cm^{-2} for $C^b =$ 1 mM, both at +200 mV. The adsorption isotherms were both found to be approximately linear; i.e., $\Gamma \propto C^b$. These values of Γ should be regarded as only approximate in view of the inevitable assumptions that are made in the single-step chronocoulometric analysis.[28]

Unfortunately, chronocoulometric measurements for these reactants at platinum and gold electrodes were unsuccessful on account of the proximity of the reduction waves to the potential of hydrogen evolution coupled with a general irreproducibility and nonideal shape of the charge–time transients. However, the adsorption of $Co(NH_3)_5pyz^{3+}$ at gold was detected from the presence of a current–potential peak for its reduction by using linear sweep voltammetry, for rapid sweep rates (>10 V s^{-1}) and small reactant concentrations ($\lesssim 0.1$ mM) where the adsorbate provides the predominant contribution to the Faradaic current.[5b,d] For $C^b = 0.1$ mM, $\Gamma \approx$ 6×10^{-11} mol cm^{-2} at 200 mV.

Discussion

Inspection of the electrochemical rate constants listed in Tables I and II reveals that substitution of the aquo ligand in $Co(NH_3)_5OH_2^{3+}$ by pyridine, pyrazine, and especially 4,4'-bipyridine yields substantial (up to ca. 10^3-fold) increases in the rate constants for reduction of these complexes at 0 mV vs. SCE at mercury, platinum, and gold electrodes. These rate data for $Co(NH_3)_5X$ reduction are also presented in Figure 1 in the form of a plot of log k_{app} as a function of the ligand X. Moreover, since the values of α_{app} at a given electrode surface are also uniformly larger for the heterocycle-containing

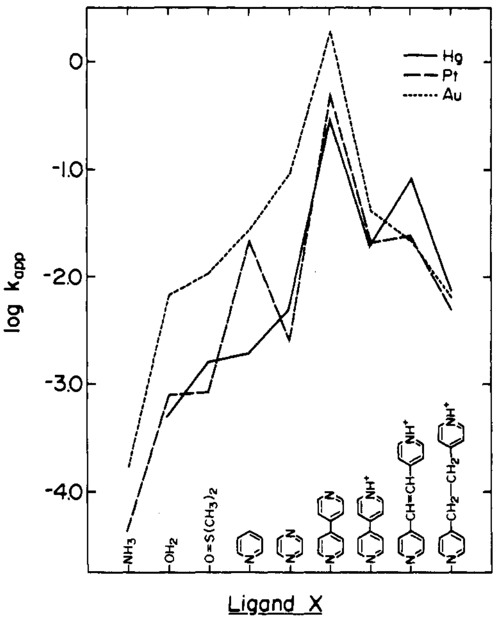

Figure 1. Plot of logarithm of apparent rate constant log k_{app} measured at 0 mV vs. SCE for reduction of various $Co^{III}(NH_3)_5X$ complexes at mercury, platinum, and gold electrodes in perchlorate electrolytes as a function of the ligand X noted on the x axis. Data are taken from Table I.

complexes, the extent of these rate increases is even larger if a more negative potential is chosen for this comparison.

It is useful to discuss such electrochemical reactivity patterns in terms of a "preequilibrium" model where electron transfer is presumed to occur via reorganization of a "precursor" complex formed from the bulk reactant in a preceding equilibrium.[3,5] We can express the rate constant k_{app} for the overall reaction as[3,5,29,30,33]

$$k_{app} = K_p \kappa \nu_p \exp(-\Delta G^*_e/RT) \qquad (2)$$

where K_p is the equilibrium constant for the preceding step, ΔG^*_e is the free energy for the elementary electron-transfer step, ν_p is a (unimolecular) frequency factor, and κ is an electronic transmission coefficient. The reorganization energy can be separated into "intrinsic" and "thermodynamic" contributions according to[3,5c]

$$\Delta G^*_e = \Delta G^*_i + \alpha[F(E - E^\circ) + RT(\ln K_p - \ln K_s)] \qquad (3)$$

where E° is the standard (or formal) electrode potential for the redox couple, K_s is the equilibrium constant for formation of the successor state (i.e., the ground state immediately following electron transfer) from the bulk product, and ΔG^*_i is the so-called intrinsic barrier. (This last quantity is the component of ΔG^*_e that remains when the free energy driving force for the elementary reaction equals zero.[3,31])

Since nitrogen donor ligands are generally expected to form thermodynamically more stable cobalt complexes than weak oxygen donors such as water, and to a greater extent for

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(33) It should be noted that the preequilibrium model embodied in eq 2 and 3 applies, at least in principle, to both inner- and outer-sphere pathways; the equilibrium constants K_p and K_s refer to the formation of an effective two-dimensional precursor or successor species at the electrode surface.[3,5,29] Such a model is therefore distinct from the collision model that is commonly applied to outer-sphere electron transfer.[30] The application of the preequilibrium model to electrochemical reactions will be discussed in detail elsewhere.

Table III. Relative Rate Comparisons between Electrochemical and Homogeneous Reductions of Various $Co^{III}(NH_3)_5X$ Complexes

	$k_{app}/k_{app}^{OH_2}$ [b]				$k_h/k_h^{OH_2}$ [c]		
complex[a]	Hg[d] (0.5 M $LiClO_4$)	Hg[e] (0.3 M KF)	Pt[d] (0.1 M $NaClO_4$)	Au[d] (0.1 M $NaClO_4$)	$Fe(CN)_6^{4-}$	Eu^{2+}	Cr^{2+}
$R-NH_3^{3+}$	6×10^{-4}	...	0.055	0.025		$0.02^{g,h}$	$\sim 1 \times 10^{-3\ n,o}$
$R-py^{3+}$	3.8	18	28	4.0	0.083^f	$1.1^{g,i}$	$\sim 0.4^{i,n}$
$R-pyz^{3+}$	10	7	33	13.5		$93^{g,j}$	$1 \times 10^{7\ i,n}$
$R-BP^{3+}$	~600	1300	640	280	0.13^f		
$R-BPA^{3+}$	...	460	...			$2.0^{g,i,k}$	$15^{i,n,k}$
$R-BPE^{3+}$	...	2000	...	...	0.055^f	$<4^{g,i,l}$	$<3^{i,n,l}$
$R-BPEH^{4+}$	165	...	31	3.3		$7^{g,m}$	

[a] For nomenclature see footnote *a* to Table I. [b] Ratio of apparent rate constant for listed complex measured at 0 mV vs. SCE to corresponding rate constant for $Co(NH_3)_5OH_2^{3+}$ reduction; taken from data listed in Tables I and II. [c] Ratio of rate constant for homogeneous reduction of listed complex to rate constant for $Co(NH_3)_5OH_2^{3+}$ reduction by reductant given at top of each column. Data refer to ionic strength $\mu \approx 1$ unless otherwise indicated and are taken from references noted. [d] k_{app} obtained at pH 1–3, adjusted with $HClO_4$. [e] k_{app} obtained in 0.3 M KF; pH adjusted to ca. 5.0 by addition of HF. [f] From ref 14 and 15. Values of k_h refer to outer-sphere electron transfer within a precursor (collision) complex, obtained at $\mu = 0.1$ ($k_h = 0.18$ s^{-1} for $Co(NH_3)_5OH_2^{3+}$ reduction). [g] $k_h = 0.075$ M^{-1} s^{-1} for $Co(NH_3)_5OH_2^{3+}$ reduction ($\mu = 1$). [h] From J. Doyle and A. G. Sykes, *J. Chem. Soc. A*, 2836 (1968). [i] From ref 16. [j] From ref 17. [k] May refer to reduction of either $R-BPA^{3+}$ or $R-BPAH^{4+}$.[25] [l] May refer to reduction of either $R-BPE^{3+}$ or $R-BPEH^{4+}$.[25] [m] From ref 18. [n] k_h for $Co(NH_3)_5OH_2^{3+}$ reduction by Cr^{2+} estimated to be 0.01 ± 0.005 M^{-1} s^{-1} (at $\mu = 0.1$) from relative rate comparison with other reductants (see R. G. Linck *MTP Int. Rev. Sci.*: *Inorg. Chem., Ser. One*, 9, 303 (1972)). [o] From A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, 83, 793 (1961).

Co(III) than for high-spin Co(II), the (albeit unknown) formal potentials for the Co(III)/(II) pentaammine couples containing nitrogen heterocycles are almost certainly more negative than for $Co(NH_3)_5OH_2^{3+/2+}$. Therefore, the overall free energy driving force $F(E - E°)$ for the former reactions will be less favorable than for $Co(NH_3)_5OH_2^{3+}$ reduction at a given electrode potential E, so the observed larger rates for these reactions are opposite to those expected on the basis of driving force considerations alone (eq 2, 3). (Since it is expected that $K_p \approx K_s$, the "surface" contribution $RT(\ln K_p - \ln K_s)$ to the driving force term in eq 3 should be small.) This suggests that the enhanced reactivity of the heterocycle-containing complexes arises instead from the observed ability of the aromatic ligands to adsorb at the electrode surface, thereby enhancing the reactant concentration (large K_p, eq 2) and/or lowering the intrinsic barrier ΔG^*_i (eq 3).

Further information on the factors responsible for the electrochemical reactivity patterns can be obtained by means of rate comparisons between corresponding heterogeneous and homogeneous reactions. According to the adiabatic electron-transfer model of Marcus and others, the ratios of the rate constants for a series of electrochemical reduction (or oxidation) reactions measured at a fixed electrode potential should be the same as the ratios of the rate constants for the corresponding homogeneous reactions using a fixed reducing (or oxidizing) agent.[32] Strictly, the rate constants need to be corrected for electrostatic work terms (or the work terms should cancel), and the thermodynamic driving forces are sufficiently small so that the work-corrected electrochemical (and chemical) transfer coefficients equal 0.5.[32] Consequently, the relationship is only expected to apply if the rate constants uniformly refer to outer-sphere pathways. Since homogeneous reduction using reagents such as $Ru(NH_3)_6^{2+}$ or $Fe(CN)_6^{4-}$ almost certainly will be outer sphere, the occurrence of electrochemical rate constants that are markedly larger than expected on the basis of this correlation provides strong evidence that a more facile reaction pathway is available for these electrode reactions.[2,5,6] Such comparisons therefore provide a means of ascertaining if the observed reactivity variations within a series of related electrochemical reactions are due to variations in thermodynamic and intrinsic factors associated with outer-sphere pathways or if they additionally reflect environmental influence associated with specific reactant–electrode interactions.

Table III consists of ratios of the apparent rate constant k_{app} for the electroreduction of a given complex at 0 mV vs. SCE at mercury, platinum, and gold surfaces with respect to the corresponding values for $Co(NH_3)_5OH_2^{3+}$ reduction, $k_{app}/k_{app}^{OH_2}$. Listed alongside for comparison are the homogeneous rate data available in the literature for the reduction of these complexes by $Fe(CN)_6^{4-}$, Eu^{2+}, and Cr^{2+}. These are also expressed as ratios of the rate constants k_h for each oxidant with respect to the values for $Co(NH_3)_5OH_2^{3+}$ reduction by the same reductant, $k_h/k_h^{OH_2}$. The values of $k_h/k_h^{OH_2}$ for reduction by $Fe(CN)_6^{4-}$ listed in Table III are obtained from unimolecular rate constants (s^{-1}) for activation within a stable ion pair formed between the reactants;[14,15] they therefore are corrected for work terms and refer to outer-sphere pathways. It is seen that the ratios $k_{app}/k_{app}^{OH_2}$ for the electroreduction of $Co(NH_3)_5py^{3+}$, $Co(NH_3)_5BP^{3+}$, and $Co(NH_3)_5BPE^{3+}$ are typically much greater than unity. In contrast, the corresponding rate ratios $k_h/k_h^{OH_2}$ for reduction by $Fe(CN)_6^{4-}$ are uniformly smaller than unity, as expected for outer-sphere pathways on the basis of the driving force considerations noted above. The reduction of $Co(NH_3)_5OH_2^{3+}$ almost undoubtedly occurs via an outer-sphere pathway in electrochemical as well as homogeneous environments.[2,7] Therefore, the markedly larger values of $k_{app}/k_{app}^{OH_2}$ compared with $k_h/k_h^{OH_2}$ for $Co(NH_3)_5py^{3+}$, and especially $Co(NH_3)_5BP^{3+}$ and $Co(NH_3)_5BPE^{3+}$, reduction provide a clear signal that an especially favorable pathway is available for the electroreduction of the heterocycle-containing complexes that does not occur with homogeneous outer-sphere reductants. The same conclusion can be reached if the rate comparisons are made with $Co(NH_3)_6^{3+}$ rather than $Co(NH_3)_5OH_2^{3+}$ reduction. Moreover, the values of $k_{app}/k_{app}^{OH_2}$ for $Co(NH_3)_5BPA^{3+}$ and $Co(NH_3)BPE^{3+}$ are larger than the corresponding values of $k_h/k_h^{OH_2}$ for reduction by Eu^{2+} and Cr^{2+}, even though these reductants may be expected to provide facile inner-sphere pathways by binding to the exposed nitrogen on the bipyridine ligands. The only system that exhibits a value of $k_{app}/k_{app}^{OH_2}$ clearly smaller than $k_h/k_h^{OH_2}$ is the reduction of $Co(NH_3)_5pyz^{3+}$ by Cr^{2+}. This result is not unexpected since Cr^{2+} is known to yield remarkably rapid inner-sphere pathways with small bridging ligands.[16]

The simplest explanation for the larger values of $k_{app}/k_{app}^{OH_2}$ than $k_h/k_h^{OH_2}$ is that the values of K_p (and K_s), i.e., the work terms (eq 2, 3), for the electroreduction of the heterocycle-containing complexes are especially favorable, yielding surface reactant concentrations correspondingly greater than for $Co(NH_3)_5OH_2^{3+}$ reduction. The detection of reactant adsorption for some of these complexes at mercury and gold electrodes indicates that there indeed are reactant concentrations at the reaction plane substantially higher than expected from electrostatic considerations.[33] Thus for $Co(NH_3)_5BPH^{4+}$ and $Co(NH_3)_5py^{3+}$, the precursor equilibrium constant K_p $(=\Gamma/C^b)^3$ equals ca. 5×10^{-5} and 2×10^{-4} cm, respectively, at +200 mV in 0.5 M $LiClO_4$. Although the values of K_p for $Co(NH_3)_5OH_2^{3+}$, $K_p^{OH_2}$, are immeasurably small, rough estimates for such outer-sphere reactants can be obtained from the relation[3] $K_p = 2r \exp(-ZF\phi_{rp})$, where r is the effective reactant radius. To a first approximation, ϕ_{rp} can be identified with the Gouy–Chapman estimate of the diffuse-layer potential ϕ_d^{GC}. For 0.5 M $LiClO_4$ at +200 mV, $\phi_d^{GC} = 0 \pm 5$ mV,[34] which yields $K_p^{OH_2} \approx 7 \times 10^{-8}$ cm. Consequently, the rate ratios $k_{app}/k_{app}^{OH_2}$ for these reactants are estimated to be enhanced by the factor $K_p/K_p^{OH_2} \approx 10^3$ as a result of reactant adsorption (eq 2). This factor roughly accounts for the disparities between the corresponding values of $k_{app}/k_{app}^{OH_2}$ and $k_h/k_h^{OH_2}$ for these reactants (Table III). It therefore seems likely that the greater reactivities of these and presumably the other heterocycle-containing complexes, relative to those of $Co(NH_3)_5OH_2^{3+}$ and other simple outer-sphere reactants, are due at least in part to enhanced reactant concentrations at the electrode surface.

Inasmuch as the electroreduction rates of the heterocycle-containing complexes are markedly larger than expected for outer-sphere pathways, it might appear reasonable to assert that inner-sphere mechanisms are being followed. By analogy with the corresponding homogeneous processes it is reasonable to regard electrochemical inner-sphere pathways as those where the reactant is attached to the electrode within the transition state for electron transfer. Such transition-state structures undoubtedly occur for the reduction of $Co^{III}(NH_3)_5X$ complexes, where X = Cl^-, Br^-, NCS^-, for example, at platinum and gold electrodes.[5] These bridging anions are known to form strong chemical bonds with the metal surface[5] that are analogous to the bonds formed between the bridging anions and a homogeneous reductant such as Cr^{2+}. A similar circumstance might be expected for the electroreduction of $Co(NH_3)_5BP^{3+}$, $Co(NH_3)_5BPE^{3+}$, $Co(NH_3)_5BPE^{3+}$, and $Co(NH_3)_5pyz^{3+}$, where a favorable inner-sphere pathway could possibly result from binding the exposed nitrogen on the aromatic ligands to the metal surface. Thus nitrogen appears to be an effective "lead-in" group, encouraging inner-sphere reductions of these complexes in homogeneous solution.[16] However, the present results suggest that such transition-state structures are not the major reason for the enhanced electrochemical reactivity of these reactants. Thus if the formation of pyridyl nitrogen–metal surface bonds provides the most facile electroreduction pathway at platinum and gold surfaces, substantial rate decreases would be expected upon the addition of iodide anions since the availability of surface coordination sites would thereby be drastically decreased.[5] In contrast, only small rate decreases or even rate increases are actually observed under these circumstances (Table I); indeed the variation of the rate constants with the nature of the coordinated ligand is similar on all three metal surfaces (Table I and Figure 1). Further, even $Co(NH_3)_5py^{3+}$ is strongly adsorbed and reduced at the metal surfaces at a rate faster than anticipated on the basis of its homogeneous reactivity relative to $Co(NH_3)_5OH_2^{3+}$ reduction, although coordinated pyridine has no available nitrogen for binding to the electrode surface.

It is therefore likely that the reactants containing pyridine-type groups are adsorbed chiefly via π or van der Waals interactions between the aromatic rings and the metal surface. Both pyridine and the pyridinium cation are strongly adsorbed at mercury over a wide range of electrode potentials in the vicinity of, and positive of, the potential of zero charge (−435 mV).[35] There is strong evidence that they are preferentially oriented either flat in order to engage in π overlap with the metal surface or, at higher coverages, on edge.[35,36] The bipyridine ligand BPE has also been found to be strongly adsorbed at mercury, and it too appears to preferentially lie flat or edgewise on the surface.[37] It seems reasonable that these ligands can still be adsorbed in a similar manner when coordinated to cobalt(III) pentaammine, thus markedly stabilizing the transition state for electroreduction of these complexes.[38]

An additional factor providing particularly favorable electrochemical reaction pathways for these systems may be a decrease in the intrinsic barrier to electron transfer arising from the orientation of the heterocyclic ligands toward the electrode surface. Evidence has been presented indicating that the homogeneous reductions of these cobalt(III) pentaammine complexes by outer-sphere reductants such as $Fe(CN)_6^{4-}$ and $Ru(NH_3)_6^{2+}$ involve approach of the reductant to the ammonia rather than the pyridine side of the Co(III).[15] The more weakly solvated electrode "reductant" may be more able to attack the hydrophobic heterocyclic ring, providing more effective electron mediation (i.e., a lower intrinsic barrier) through the pyridine group than via the ammonia ligands.

Since the aromatic ligands probably displace inner-layer water molecules upon adsorption, such electrochemical reaction pathways could be designated "inner sphere". However, there is a significant difference between such heterogeneous pathways and conventional homogeneous inner-sphere mechanisms in that the former involve inherently delocalized interactions between the "bridging" ligand and the metal surface, whereas the latter usually involve the formation of a single bond between a suitable functional group on the bridging ligand and the coreactant redox center. The ability of a metal surface to engage in electron transfer with reactants containing aromatic ligands may then be determined primarily by the subtle stereochemical factors that control the adsorption thermodynamics of such species.[39] These factors are presumably responsible for the relative insensitivity of the reduction kinetics to the nature of the electrode and also the insensitivity of the rate response to change in the potential profile across the double layer to the presence of the heterocyclic ligand (Table II). Such behavior has been previously considered to be indicative of outer- rather than inner-sphere mechanisms;[1,2,5] in particular, the kinetics of anion-bridged electrochemical pathways can be extremely sensitive to the nature of the electrode surface.[5] Consequently, the experimental, and even conceptual, distinction between inner- and outer-sphere electrode reactions could well become blurred when such delocalized ligand–surface interactions can occur.

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Registry No. $R-OH_2^{3+}$ (R = $Co^{III}(NH_3)_5$), 14403-82-8; $R-NH_3^{3+}$, 14695-95-5; $R-Me_2SO^{3+}$, 44915-85-7; $R-py^{3+}$, 31011-67-3; $R-pyz^{3+}$, 59389-55-8; $R-BP^{3+}$, 53879-90-6; $R-BPH^{4+}$, 82065-76-7; $R-BPAH^{4+}$, 82065-77-8; $R-BPEH^{4+}$, 74911-57-2; Hg, 7439-97-6; Pt, 7440-06-4; Au, 7440-57-5.

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