are no low-lying vacant orbitals on the bound N atoms of the hexaaza cages to effect such an exchange. In addition, the possibility that electron transfer is implemented through the N cap in the sepulchrate system has been addressed elsewhere[6] and found not to be viable. Overall, the body of evidence is pointing to the internal reorganization energies as a dominating factor in the electron-transfer rates for these systems.

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# Redox Reactions of Variable-Spin Six-Coordinate Bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) Complexes

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The effect of spin state on the electron-transfer properties of the variable-spin six-coordinate bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) family, where R = C(CH$_3$)$_3$, CH(CH$_3$)$_2$, *p*-PhCH$_3$, and CH$_2$Ph, was investigated in nonaqueous media. Both Co$^{3+}$/Co$^{2+}$ and Co$^{2+}$/Co$^+$ electrode reactions were studied. For a given complex, reversible half-wave potentials were linearly related to both the solvent dielectric constant and the solvent parameter β (a measure of solvent hydrogen-bonding acceptor ability). All heterogeneous electron-transfer rate constants were in the range (2–4) × 10$^{-2}$ cm/s and did not vary with spin state of the Co(II) complex. A similar lack of correlation was also observed between the substituent constant on the ligand and the rate constant or half-wave potential for electrooxidation–reduction. However, some correlation did exist between this substituent constant and the magnetic moment of the central Co(II) ion.

## Introduction

In a recent series of papers, we have been investigating the effect of spin state and spin equilibria on the redox reactions of iron(III) and iron(II) complexes.[1-4] In these studies we have shown that a relationship can sometimes be observed between the iron spin state and standard heterogeneous rates of electron transfer[2,3] but that this is not necessarily a general rule.[4] In this work we wish to report similar studies for electrode reactions involving Co(II)$_{hs⇌ls}$/Co(I)$_{hs}$ and Co(II)$_{hs⇌ls}$/Co(III)$_{ls}$ couples. No information presently exists in the literature for redox reactions of cobalt(II) spin-equilibria complexes, and thus, this study provides an interesting comparison with our previous results for Fe(III) and Fe(II) spin equilibria.

We have chosen for our investigation the six-coordinate bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes with substituents R = C(CH$_3$)$_3$, CH(CH$_3$)$_2$, *p*-PhCH$_3$, and CH$_2$Ph. These complexes, whose general structure is shown in Figure 1, were earlier shown to exhibit a $^2$E(ls) ⇌ $^4$T(hs) spin-equilibrium process in both the solid and solution states.[5] Our present interest in these compounds focuses on both the oxidation of Co(II) to yield Co(III) and the reduction of Co(II) to yield Co(I) according to Scheme I. Similar to our earlier studies involving iron complexes,[1-4] we have investigated the oxidation–reduction behavior of these species as a function of solvent, the ligand substituent, and spin state of the cationic cobalt(II) complex.

## Experimental Section

**Chemicals.** The bis(N-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes, shown in Figure 1, where R = C(CH$_3$)$_3$, CH(CH$_3$)$_2$, *p*-PhCH$_3$, and CH$_2$Ph, were synthesized as previously reported.[5] Solvents utilized were methylene chloride (CH$_2$Cl$_2$), ethylene chloride (EtCl$_2$), acetone ((CH$_3$)$_2$CO), acetonitrile (CH$_3$CN), dimethylformamide (DMF), dimethylacetamide (DMA), butyronitrile (PrCN), benzonitrile (PhCN), pyridine, and dimethyl sulfoxide (Me$_2$SO) and were of reagent grade. Methylene chloride and ethylene chloride were distilled over P$_2$O$_5$. Acetone and acetonitrile were dried over molecular sieves and then distilled. All other solvents were dried and stored over

## Scheme I
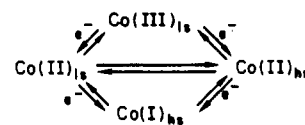


molecular sieves before utilizing. For electrochemistry, each solvent was made with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The TBAP was recrystallized from an ethyl acetate–ether mixture and dried under reduced pressure. The same solution conditions were used for the solution magnetic moment measurements as were used for the electrochemistry.

**Instrumentation.** Polarographic measurements were made on an EG&G Princeton Applied Research Model 174 polarographic analyzer or an EC Model 225 voltammetric analyzer utilizing a three-electrode geometry. The working electrode consisted of either a platinum-button electrode or a dropping-mercury electrode (DME). A commercial saturated calomel electrode (SCE) was used as the reference electrode, and a platinum wire was used as the counterelectrode. The reference electrode was separated from the bulk of the solution by a bridge with the same solvent and supporting electrolyte. The total volume utilized was 5–10 mL. Cobalt(II) complex concentrations were 10$^{-3}$–10$^{-4}$ M. Potentials were also measured with respect to the ferrocene/ferrocenium (Fc$^+$/Fc) couple in order to correct for differences in liquid-junction potential between different solvents.

Cyclic voltammetric sweep rates were between 0.2 and 5 V/s. The standard electron-transfer rate constants, $k_s$, were obtained by the method of Nicholson.[6] In this method, shifts of the peak potentials from the reversible value of 60 mV are considered quasi-reversible, and under these conditions the rate of electron transfer can be calculated from eq 1,[6] where $k_s$ is the heterogeneous electron-transfer

$$k_s = \frac{\Psi}{\gamma^\alpha}\left(\frac{nFv\pi D}{RT}\right)^{1/2} \qquad (1)$$

rate constant (cm/s), $n$ is the number of electrons transferred in each step, $v$ is the potential sweep rate (V/s), $D$ is the diffusion coefficient

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[†] University of Houston.
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Table I. Half-Wave Potential for Oxidation and Reduction of Compound II in Different Solvents Containing 0.1 M TBAP at 25 °C

| no. | solvent | dielectric constant,[a] $\epsilon$ | $\beta$,[b] cm$^{-1}$ × 10$^3$ | Co$^{3+}$/Co$^{2+}$ | | Co$^{2+}$/Co$^+$ | | Co$^+$/Co$^+$ radical | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $E_{1/2}$, V (vs. SCE) | $E_{1/2}$, V (vs. Fc$^+$/Fc) | $E_{1/2}$, V (vs. SCE) | $E_{1/2}$, V (vs. Fc$^+$/Fc) | $E_{1/2}$, V (vs. SCE) | $E_{1/2}$, V (vs. Fc$^+$/Fc) |
| 1 | CH$_2$Cl$_2$ | 8.9 | 0.00 | 0.66 | 0.17 | -0.33 | -0.82 | -1.41 | -1.90 |
| 2 | EtCl$_2$ | 10.4 | 0.00 | 0.67 | 0.18 | -0.35 | -0.84 | -1.44 | -1.93 |
| 3 | py | 12.4 | 0.64 | 0.66 | 0.13 | -0.33 | -0.86 | -1.32 | -1.85 |
| 4 | (CH$_3$)$_2$CO | 20.7 | 0.48 | 0.60 | 0.10 | -0.37 | -0.87 | -1.33 | -1.83 |
| 5 | PhCN | 25.2 | 0.41 | 0.66 | 0.16 | -0.38 | -0.86 | -1.40 | -1.88 |
| 6 | DMF | 36.7 | 0.69 | 0.52 | -0.03 | -0.40 | -0.95 | -1.34 | -1.89 |
| 7 | CH$_3$CN | 37.5 | 0.31 | 0.56 | 0.16 | -0.48 | -0.88 | -1.48 | -1.88 |
| 8 | DMA | 37.8 | 0.76 | 0.57 | 0.02 | -0.38 | -0.93 | -1.35 | -1.90 |
| 9 | Me$_2$SO | 46.7 | 0.76 | 0.50 | 0.04 | -0.42 | -0.92 | -1.38 | -1.88 |

[a] Reference 9. [b] Reference 10.
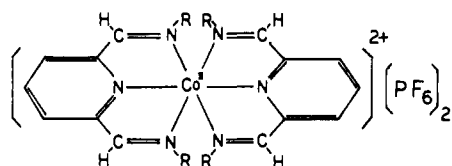


Figure 1. Structure of bis(*N*-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes where R represents the following substituents: I, C(CH$_3$)$_3$; II, CH(CH$_3$)$_2$; III, *p*-PhCH$_3$; IV, CH$_2$Ph.
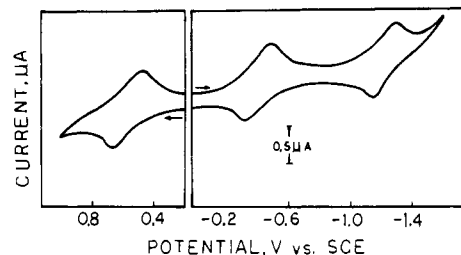
of the reacting species, $\gamma = (D_o/D_r)^{1/2}$ (where $D_o$ is the diffusion coefficient of the oxidized form of the reactant and $D_r$ is the diffusion coefficient of the reduced form of the reactant), $\alpha$ is the transfer coefficient, and $\pi$, $F$, $R$, and $T$ have their usual significance. $\Psi$ is related to $\Delta E$, the potential difference between the cathodic and anodic peak potentials. Values of $\Psi$, as defined by eq 1 for various values of $\Delta E_p$, have been tabulated after the solution of the appropriate equations by numerical analysis.[6] Values of diffusion coefficients were calculated from the Randles–Sevcik equations at slow scan rates or from the dc polarograms, and values of (1.1–1.3) × 10$^{-5}$ cm$^2$/s were obtained for all of the complexes investigated in this series. Similar values of $D$ were obtained by the two techniques. Confirmation that $D_o = D_r$ was obtained from the virtually identical values of $i_{pa}$ and $i_{pc}$.

Generally, organic solvents possess relatively high resistances. Therefore, special precautions were taken with these solvents in order to eliminate or minimize potential shifts due to uncompensated *iR* loss. In this work, a Luggin capillary was employed and positive feedback was utilized. In addition, a small working-electrode area (0.7 mm$^2$) and a low compound concentration were utilized in order to minimize the peak current and thus the *iR* loss. The overall number of electrons transferred was determined by controlled-potential coulometry using a Princeton Applied Research Model 173 potentiostat/galvanostat with a Model 179 digital coulometer. A relatively large-area platinum-gauze electrode and a large coiled platinum-wire electrode were used as the anode and cathode for controlled-potential electrolysis.
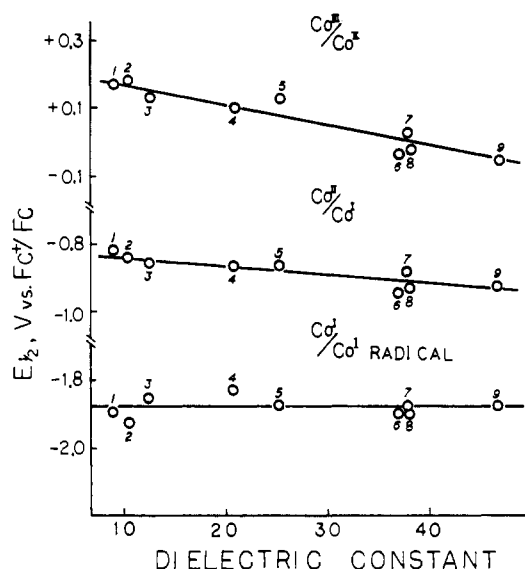
Magnetic susceptibilities in solution were measured on a Varian A-60A analytical NMR spectrometer at room temperature by the Evans method.[7,8] Me$_4$Si was utilized as the inert reference compound. Pascal's constants were used to correct the diamagnetism for ligands and PF$_6^-$ in 10$^{-6}$ cgsu: compound I, -417; compound II, -395; compound III, -505; compound IV, -500; PF$_6^-$, -64.[5]

**Results and Discussion**

**Solvent Effects on Half-Wave Potentials.** All four of the compounds in Figure 1 exhibited two reversible reductions, while three of the compounds (II–IV) exhibited reversible oxidations on the cyclic voltammetry time scale. This is illustrated in Figure 2 for the electrode reactions of compound II in acetone/0.1 M TBAP. The electrode reactions at +0.60 and -0.37 V vs. SCE may be assigned as the oxidation and reduction of Co(II) to yield Co(III) and Co(I) complex, re-

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Figure 2. Cyclic voltammogram of compound II in acetone/0.1 M TBAP (scan rate = 100 mV/s).



Figure 3. Plots of $E_{1/2}$ vs. dielectric constant for the three electrode reactions of compound II in acetone/0.1 M TBAP. Numbers correspond to solvents given in Table I.

spectively. The reaction at more negative potentials (-1.33 V for compound II) may be assigned as a reduction to form the anion radical of Co(I).

Half-wave potentials were measured for each complex in up to nine electrochemical solvents. In all solvents the waves remained reversible but were slightly shifted along the potential axis as a function of the specific solvent. This is shown by the data in Table I, which lists the potentials for oxidation and reduction of compound II vs. SCE and vs. the Fc$^+$/Fc couple (which corrects for liquid-junction potential).

The bis(*N*-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes investigated are all six-coordinate, being derived from two tridentate strong-field ligands. Therefore, it is unlikely that the solvent participates in ligation reactions in these complexes. Examination of Table I and the cyclic voltammograms of these complexes reveals no significant differences in the half-wave potentials between nonbonding solvents,
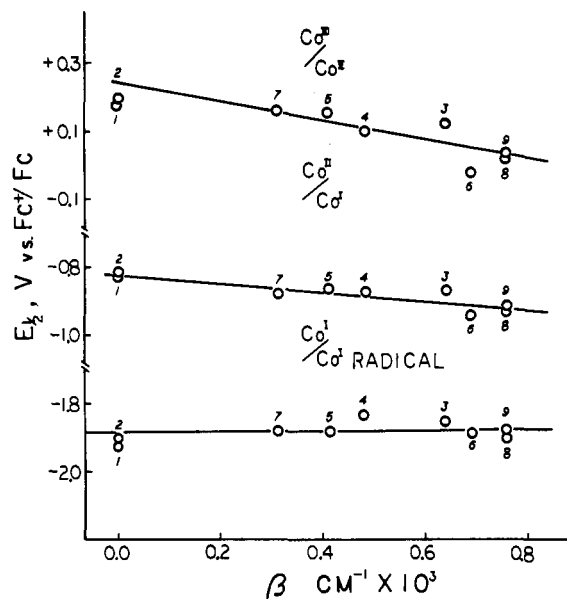
**Figure 4.** Plots of $E_{1/2}$ vs. $\beta$ values for the three electrode reactions of compound II in acetone/0.1 M TBAP. Numbers correspond to solvents given in Table I.

weakly bonding solvents, and strongly bonding solvents. Diagnostic plots of $E_{1/2}$ (corrected for liquid-junction potential) vs. the dielectric constant and $E_{1/2}$ vs. $\beta$ values (a measure of solvent hydrogen-bonding acceptor ability[10]) for the three electrode reactions of compound II are presented in Figures 3 and 4, respectively, where the numbers correspond to the solvents listed in Table I. Values of dielectric constants are taken from Sawyer et al.,[9] while those for $\beta$ are taken from Kamlet et al.[10]

Most of the dipolar aprotic solvents utilized in this study have appreciable Lewis-base character and thus solvate cations better than anions. From Figure 3, it can be seen that the Co(II) compound becomes easier to oxidize and harder to reduce as the dielectric constant increases. The $\beta$ scale is a measure of solvent hydrogen-bonding acceptor ability[10] and has been shown to be applicable to a generalized quantitative treatment of pure solvent effects related by hydrogen bonding. Figure 4 illustrates that solvents with larger $\beta$ values favor stabilization of the higher oxidation state over that of the lower one. Because of this enhancement, potentials for both the $Co^{3+}/Co^{2+}$ and $Co^{2+}/Co^{+}$ couples are shifted toward more negative values with increase in the value of $\beta$. It is interesting to note that the metal-centered oxidation is both $\beta$ and dielectric constant dependent, while that for anion radical formation is independent of both parameters. The Co(II)/Co(I) reaction is only slightly dependent on the solvent parameters.

A similar solvent dependence has been noted for the Fe(III)/Fe(II) reaction of the $[Fe^{III}(X\text{-}Sal)_2trien]^+$ spin-equilibrium system,[1] even though both compounds are six-coordinate and thus cannot be effected by direct solvent–metal interactions. In the present series of compounds, hydrogen bonding through the imine hydrogens seems to be the probable means of manifesting these solvent effects. A similar but much larger solvent effect was also observed for the Co(II)/Co(III) reaction of (TPP)Co.[11] In this case, however, the Co(II) form of the complex is four- or five-coordinate while that of Co(III) is six-coordinate. This change of coordination number upon oxidation thus produces a much stronger effect of solvent on the redox reactions.

**Table II.** Magnetic Moments and Half-Wave Potentials for the Bis(*N*-R-2,6-pyridinedicarboxaldimine)cobalt(II) Complexes in Acetone/0.1 M TBAP at 25 °C

| | $\mu_{eff}$, $\mu_B$ | | | half-wave potential, V (vs. SCE) | | |
|---|---|---|---|---|---|---|
| compd | 0.1 M TBAP | lit[a] | $4\sigma$ | $Co^{3+}/Co^{2+}$ | $Co^{2+}/Co^{+}$ | $Co^{+}/Co^{+}$ radical |
| I | 5.3 | 5.2 | $-0.80^b$ | e | -0.36 | -1.22 |
| II | 4.2 | 4.1 | $-0.60^b$ | 0.60 | -0.37 | -1.33 |
| III | 3.9 | 4.0 | $+0.04^{b,c}$ | 0.77 | -0.23 | -1.10 |
| IV | $3.3^a$ | 3.3 | $-0.36^d$ | 0.55 | -0.45 | -1.34 |

[a] Reference 5, measured in absence of supporting electrolyte. [b] Reference 11. [c] Value of $\sigma$ was for benzene rather than methylbenzene. [d] Exher, O. *Collect. Czech. Chem. Commun.* **1966**, *31*, 65. [e] No reaction observed.

It should be noted that $\beta$ is very similar to the solvent donor number parameter (DN), which has often been utilized to correlate potentials in different solvents.[12] However, the relationship between $E_{1/2}$ and DN or between $E_{1/2}$ and $\beta$ is not a simple one[13] and will depend on the specific coordination chemistry of each species involved in the redox reaction. In this specific study all of the cobalt complexes are six-coordinate (see Figure 1), and thus solvent effects on half-wave potentials are not related to direct bonding interactions.

**Substituent Effects on Half-Wave Potentials.** Experimentally obtained half-wave potentials for the three-electrode reactions of all four compounds in acetone/0.1 M TBAP are listed in Table II. Also included in this table are the relevant substituent constants of each complex, $4\sigma$, and the measured magnetic moment of the cobalt(II) complex with and without supporting electrolyte. The magnetic measurements, made only at room temperature, were performed to ensure that the magnetic properties under the present experimental conditions (where the solutions contained 0.1 M TBAP) were the same as those reported previously and such was found to be the case. As seen in this table, $\mu_{eff}$ for a given complex of cobalt(II) is independent of ionic strength. A comparison of the data in Table II also indicates a significant difference in the magnetic moment on going from compound I to compound IV. Compound I, R = $C(CH_3)_3$, remains high-spin in solution ($\mu_{eff}$ = 5.3 $\mu_B$; 100% hs), while compound IV is mainly low-spin ($\mu_{eff}$ = 3.3 $\mu_B$; 74% ls) under the same solution conditions at 25 °C.

Generally, electron-donating groups produce an easier oxidation and a more difficult reduction while electron-withdrawing groups have the opposite effect. Under these conditions the shift of half-wave potentials should be related to the value of $\sigma$ by the linear free energy relationship $\Delta E_{1/2} = \sigma\rho$.[14] As seen in Table II, $E_{1/2}$ varied substantially but not monotonically as a function of substituent, R (and $\sigma$), while a constant difference ($\sim 1.0$ V) was maintained between the first oxidation and the first reduction potential of each compound. This lack of a definite trend is shown in Figure 5b, which plots $E_{1/2}$ vs. $4\sigma$ for the $Co^{2+}/Co^{+}$ reaction of the bis(*N*-R-2,6-pyridinedicarboxaldimine)cobalt(II) complexes in acetone/0.1 M TBAP. A similar lack of correlation is also observed for the $Co^{3+}/Co^{2+}$ and $Co^{+}/Co^{+}$ radical reactions.

**Rates of Electron Transfer.** A typical cyclic voltammogram obtained in acetone is shown in Figure 2. For each of the four complexes the peak separation was greater than the theoretical 60 mV and increased with scan rate. Thus, from these data and an experimentally determined diffusion coefficient of (1–3) × $10^{-5}$ cm²/s, values of $k_s$ could be calculated by using eq 1.

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**Table III.** Electrochemical Data Used in the Calculation of the Electron-Transfer Rate Constants for Oxidation of Compound IV in Acetone/0.1 M TBAP at 25 °C

| reaction | scan rate, $v$, V/s | $i_p$, $\mu$A | $i_p/v^{1/2}$, $\mu$A s$^{1/2}$/V$^{1/2}$ | $E_{p,c}$, V | $E_{p,a}$, V | $\Delta E_p$, mV | $\Psi^c$ | $k_s$, cm/s |
|---|---|---|---|---|---|---|---|---|
| $Co^{3+}/Co^{2+}$ $^a$ | 1.5 | 0.32 | 0.262 | 0.545 | 0.658 | 115 | 0.40 | $2.1 \times 10^{-2}$ |
| | 2.0 | 0.37 | 0.262 | 0.538 | 0.668 | 130 | 0.32 | $1.9 \times 10^{-2}$ |
| | 2.5 | 0.42 | 0.265 | 0.534 | 0.672 | 138 | 0.30 | $2.0 \times 10^{-2}$ |
| | 3.0 | 0.46 | 0.265 | 0.529 | 0.677 | 148 | 0.29 | $2.1 \times 10^{-2}$ |
| $Fc^+/Fc$ $^b$ | 1.5 | 1.55 | 1.27 | 0.484 | 0.558 | 74 | 1.73 | 0.11 |
| | 2.0 | 1.85 | 1.31 | 0.482 | 0.560 | 78 | 1.38 | 0.10 |
| | 2.5 | 2.10 | 1.32 | 0.481 | 0.561 | 80 | 1.21 | 0.10 |
| | 3.0 | 2.30 | 1.32 | 0.479 | 0.563 | 84 | 1.05 | 0.10 |

$^a$ Calculated for a 0.20 mM concentration with a diffusion coefficient of $1.3 \times 10^{-5}$ cm/s. $^b$ Calculated for a 0.16 mM concentration with a diffusion coefficient of $3.0 \times 10^{-5}$ cm/s. $^c$ Reference 6.
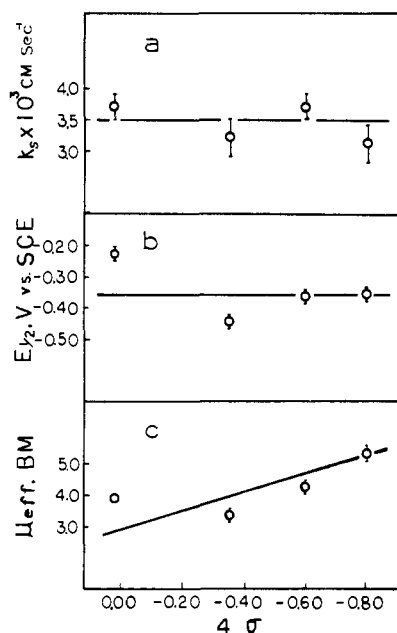


**Figure 5.** Plots of $k_s$, $E_{1/2}$, and $\mu_{eff}$ vs. $4\sigma$ for the electrode reaction Co(II) $\rightleftarrows$ Co(I). The four compounds are identified in Table I.

Typical data for the determination of the heterogeneous rate constants of compound IV and of the $Fc^+/Fc$ couple are shown in Table III. It can be seen that, for each reaction, a constant and self-consistent rate constant is obtained. In this table the heterogeneous electron-transfer rate constants are presented to only two significant figures, because of the uncertainty in measuring the trace on the pictures taken from the Polaroid camera to better than 1 or 2 mV.

Table IV gives both the magnetic properties of each cobalt(II) complex and a summary of the measured rate constants for the electron-transfer reaction. Examination of Tables II and IV shows that there is no obvious correlation between $E_{1/2}$ and $k_s$. In addition, standard heterogeneous electron-transfer rate constants for each electrode reaction do not seem to correlate with changes in the ligand substituent or the magnetic moment and, therefore, the high- and low-spin isomer populations of the cobalt(II) form. This is shown graphically in Figure 5, which plots $k_s$, $E_{1/2}$ (vs. SCE), and $\mu_{eff}$ vs. $\sigma$ for each $Co^{2+}/Co^+$ couple where the $Co^+$ products should be high-spin species. Similar invariant values of $k_s$ and $E_{1/2}$ were also obtained for the $Co^{3+}/Co^{2+}$ couples (Table IV), where all the $Co^{3+}$ products are undoubtedly low spin. Because

**Table IV.** Electron-Transfer Rate Constants for the Bis($N$-R-2,6-pyridinedicarboxaldimine)cobalt(II) Complexes in Acetone/0.1 M TBAP at 25 °C

| | | | $k_s$, cm/s | |
|---|---|---|---|---|
| compd | $\mu_{eff}$, $\mu_B$ | % hs$^b$ | $Co^{3+}/Co^{2+}$ | $Co^{2+}/Co^+$ |
| I | 5.3 | 100 | $c$ | $3.1 \times 10^{-2}$ |
| II | 4.2 | 55 | $1.7 \times 10^{-2}$ | $3.7 \times 10^{-2}$ |
| III | 3.9 | 43 | $2.1 \times 10^{-2}$ | $3.7 \times 10^{-2}$ |
| IV | 3.3$^a$ | 26 | $2.0 \times 10^{-2}$ | $3.2 \times 10^{-2}$ |

$^a$ Reference 5; measured in the absence of supporting electrolyte. $^b$ Calculated by assuming high-spin (hs) and low-spin (ls) magnetic moments of 5.3 and 2.2 $\mu_B$, respectively. $^c$ No reaction observed.

of this invariance in $k_s$ within both the $Co^{3+}/Co^{2+}$ and $Co^{2+}/Co^+$ redox series, $k_s$ values were also determined for the $Fc^+/Fc$ couple. As shown in Table III, the electron-transfer rate for the $Fc^+/Fc$ couple was found to be 1 order of magnitude faster than for any of the cobalt processes, diminishing the possibility that uncompensated solution resistance is responsible for a "leveling effect" where all electron-transfer reactions might appear to have equivalent rates in these nonaqueous solvents. Thus, we are left with a somewhat inconclusive and unexpected result for the present cobalt(II) spin-equilibrium system, in that no substantial change is observed in $k_s$ as a function of the cobalt(II) spin state. This result is contrary to that which we found earlier for the $[Fe^{III}(X-Sal)_2trien]^+$ spin equilibrium system[2] where $k_s$ varied smoothly as a function of the high- and low-spin isomer populations, but it is reminiscent of our more recent results obtained for the $[Fe^{II}(6-Mepy)_3tren]^{2+}$ system[3] and for a series of bisligated $Fe^{III}$ octaethyl- and tetraphenylporphyrin complexes in nonaqueous media[4] where $k_s$ did not correlate well with spin state. Clearly, in view of these few, seemingly conflicting results, the interrelationship between redox potentials, heterogeneous electron-transfer rates, and the metal-centered spin state remains a strong challenge for both practical and theoretical electrochemistry.

**Registry No.** I(PF$_6$)$_2$, 60676-11-1; I$^{3+}$, 86350-19-8; I$^+$, 86350-23-4; II(PF$_6$)$_2$, 60645-71-8; II$^{3+}$, 86350-20-1; II$^+$, 86350-24-5; III(PF$_6$)$_2$, 60645-75-2; III$^{3+}$, 86350-21-2; III$^+$, 86350-25-6; IV(PF$_6$)$_2$, 60686-60-4; IV$^{3+}$, 86350-22-3; IV$^+$, 86350-26-7.