intensities remain almost unchanged and no new peaks arise in the course of the transformation. However, both the peak positions and the lattice spacings derived therefrom show a temperature shift that conforms to that of the high-spin fraction $n_{^5\mathrm{T}_2}$ (cf. Figure 6). These results may be rationalized if the distribution of the two spin isomers within the lattice is considered. Thus a single X-ray diffraction pattern will indeed be found, if a random distribution of the minority constituent within the majority phase is assumed. On the other hand, different and individual diffraction patterns for the two phases will be expected, if a narrow distribution of the minority phase, accompanied by pronounced domain formation, is assumed. This is apparently the situation that is encountered for spin transitions of the discontinuous type.

For the present compounds, and for $[Fe(bts)_2(NCS)_2]$,[10] then, a wide distribution of the minority constituent within the majority phase may be assumed. Apparently the high-spin $^5T_2$ and low-spin $^1A_1$ species together constitute a system that is akin to that of a solid solution of two components. It is not unlikely that the interpretation offered here may be applicable to all spin transitions of the continuous type. Additional investigations are in progress.

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Registry No. $[Fe(4\text{-}paptH)_2](ClO_4)_2$, 86527-11-9; $[Fe(4\text{-}paptH)_2](BF_4)_2$, 49731-99-9.

Contribution from the Research School of Chemistry,
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Rapid Electron Self-Exchange Involving Low-Spin Cobalt(II) and Cobalt(III) in an Encapsulated Cage Complex

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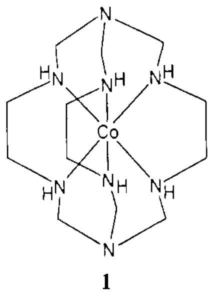
The electron self-exchange rate between the Co(II) and Co(III) macrobicyclic cage complexes of azacapten (8-methyl-1,3,13,16-tetraaza-6,10,19-trithiabicyclo[6.6.6]eicosane) has been measured by the NMR line-broadening technique (k_2 = 4500 (±300) $M^{-1}\ s^{-1}$ at 25 °C). The activation parameters are $\Delta H^* = 7\ (\pm 3)$ kcal mol^{-1} and $\Delta S^* = -18\ (\pm 11)$ cal $deg^{-1}\ mol^{-1}$. The magnetic moments for the Co(II) complex are slightly different in the crystal lattice (1.89 μ_B) and solution (2.35 μ_B), but both indicate the Co(II) ion is largely in the low-spin condition ($t_{2g}^6e_g^1$). The large rate constant is consistent with this low-spin condition in both the Co(II) and the Co(III) ions and the consequently reduced bond lengths and therefore reduced reorganization energy relative to those of the $Co(NH_3)_6^{2+/3+}$, $Co(en)_3^{2+/3+}$, and $Co(sep)^{2+/3+}$ ions.

Introduction

The chemistry of a number of complexes in which cobalt(III) and cobalt(II) ions are effectively encapsulated within a macrobicyclic ligand framework has been reported previously.[1-3] The tightly bonding nature of these cage ligands ensures the nonlability of the cobalt(II) species. In fact, it is possible to isolate chiral cobalt(II) cage complexes.[1-3] Two such macrobicyclic cage systems are the octaaza $[Co(sep)]^{3+/2+}$ (**1**)[1] and the nitrogen–sulfur $[Co(azacapten)]^{3+/2+}$ (**2**)[3] complexes.



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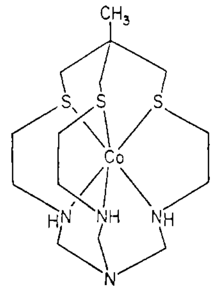

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The inert octahedral nature of these and other similar cage complexes ensures that reactions involving the cobalt(II) species occur in the absence of ligand–metal exchange.[1-3] As a consequence, a reaction involving the exchange of an electron between the Co(II) and Co(III) states must occur via a pathway not involving ligand exchange and presumably follows an outer-sphere path (eq 1).[4]

$$^*Co(azacapten)^{3+} + Co(azacapten)^{2+} \rightleftharpoons {}^*Co(azacapten)^{2+} + Co(azacapten)^{3+} \quad (1)$$

The electron self-exchange rates of a series of such complexes have been studied previously with use of a polarimetric technique.[5,6] A preliminary investigation of the sulfur–nitrogen cage indicated a rate of self-exchange too rapid to be measured by this method. The present paper explores measurements of the electron-transfer rate by an NMR line-broadening technique.

Experimental Section

All manipulations involving solutions of the cobalt(II) complexes were performed under an atmosphere of nitrogen that had been scrubbed with solutions of Cr^{2+}. Aqueous solutions of the oxygen-sensitive cobalt(II) complexes were transferred under a positive pressure of oxygen-free nitrogen with stainless steel transfer tubing.

Commercial CF_3SO_3H (3M Co.) was distilled before use.

^1H NMR spectra were recorded in D_2O solution relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard, except as described.

$[Co(azacapten)]Cl_3$ was prepared as described previously[3] and isolated as its triflate ($CF_3SO_3^-$) salt with use of CF_3SO_3H. The

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cobalt(II) cage complex was isolated as its $CF_3SO_3^-$ or $S_2O_6^{2-}$ salt after reduction of an aqueous solution of the cobalt(III) complex over zinc amalgam and addition to solid $NaCF_3SO_3$ or LiS_2O_6. When the resultant solution was cooled, a purple crystalline solid deposited. The solution was filtered under a nitrogen stream and dried in vacuo. Anal. Calcd for $C_{14}H_{30}N_4S_3Co(S_2O_6)$: C, 29.51; H, 5.32; N, 9.84; S, 28.14. Found: C, 29.7; H, 5.3; N, 9.7; S, 28.3. Visible spectrum (λ_{max}, nm (ϵ_{max}) in H_2O): 500 (124), 550 sh (104), 780 br (30). Solutions of the purple cobalt(II) complex were prepared by the quantitative reduction of the cobalt(III) complex with zinc amalgam. D_2O solutions of the cobalt(III) and cobalt(II) complexes were thoroughly purged with O_2-free nitrogen before mixing. The resulting solution was transferred under positive pressure of nitrogen into a previously nitrogen-purged 10-mm NMR tube, and after partial evacuation of the nitrogen atmosphere, the tube was sealed. Tetramethylammonium triflate (TMAT) was employed as an internal reference. The solution in the sealed tube deposited fine purple needles of the cobalt(II) complex on standing at room temperature; however, when they were warmed, these dissolved to give the original purple-red solution of the cobalt(II/III) mixture.

The ^1H NMR spectra were recorded with a JEOL FX60 spectrometer in the FT mode. The spectrometer was equipped with a variable-temperature unit. Accumulation times at each temperature varied from 30 to 60 min, depending on concentration and exchange broadening. The temperature range studied was from +3 to +43 °C. In the exchange experiments, a pulse width of 20 μs (60°) and pulse delays of 1 s were used. That these conditions allowed adequate times for relaxation between pulses was checked in a series of preliminary experiments, which used pulse delays ranging up to 10 s.

The magnetic susceptibility of the purple complexes $[Co(azacapten)](CF_3SO_3)_2$ and $[Co(azacapten)](S_2O_6)$ was measured by the Faraday method on a Newport Instruments single-temperature Gouy balance with a Faraday kit conversion as supplied. Solid $Hg[Co(CNS)_4]$ was used as calibrant at 294 K. Diamagnetic corrections for the complex were calculated by using Pascal's constants.[7]

The solution magnetic susceptibility of the cobalt(II) cage was measured in D_2O solution with use of the Evans ^1H NMR method[8] and a JEOL PMX60 spectrometer, probe temperature 28 °C. A solution of the $[Co(azacapten)](CF_3SO_3)_3$ complex in D_2O solution was reduced over zinc amalgam under an O_2-free nitrogen stream and transferred into a previously degassed 5-mm NMR tube containing a sealed D_2O capillary. The concentration of the cobalt(II) solution was determined from the visible spectrum of the corresponding cobalt(III) cage after quantitative oxidation of the solution with dioxygen.

The electron-transfer cross-reaction between $[Co(azacapten)]^{3+}$[3] and the hexaamine cage complex $[Co(diamsarH_2)]^{4+}$[9] was also studied under pseudo-first-order conditions with a Cary 118 spectrophotometer at 474 nm. The cobalt(II) hexaamine complex was prepared by reduction of the cobalt(III) cage[2] with zinc amalgam under an atmosphere of purified nitrogen (μ = 0.2 M (HCl)). A solution of the $[Co(azacapten)]^{3+}$ complex was degassed with O_2-free nitrogen prior to use (μ = 0.2 M (NaCl)). The two solutions were mixed in a stopped-flow reactor, and the change in absorbance with time of the resulting solution was followed.

Results

Addition of a purple solution of the cobalt(II) cage complex $[Co(azacapten)]^{2+}$, obtained by reduction of the corresponding cobalt(III) complex with zinc amalgam, under oxygen-free conditions, to excess sodium triflate or lithium dithionate resulted in the crystallization of the paramagnetic complexes $[Co(azacapten)](CF_3SO_3)_2$ or $[Co(azacapten)](S_2O_6)$. In the solid state at 25 °C both of these complexes exhibited magnetic moments indicative of low-spin cobalt(II) with 1.89 μ_B. In D_2O solution the magnetic moment for the $[Co(azacapten)](CF_3SO_3)_2$ complex was found to be 2.35 μ_B at 28 °C.

The kinetic measurements for the electron transfer between $[Co(azacapten)]^{2+}$ and $[Co(azacapten)]^{3+}$ were determined in D_2O solution with use of an NMR line-broadening technique. The measurements focused on the proton resonance of the methyl group at the carbon cap, which for the diamagnetic cobalt(III) complex occurred at 1.4 ppm and was well separated from other proton resonances in this complex. The signal for the corresponding methyl group of the cobalt(II) cage occurred even further upfield (Figure 1). It was therefore possible to obtain accurate rate data from two site simulations

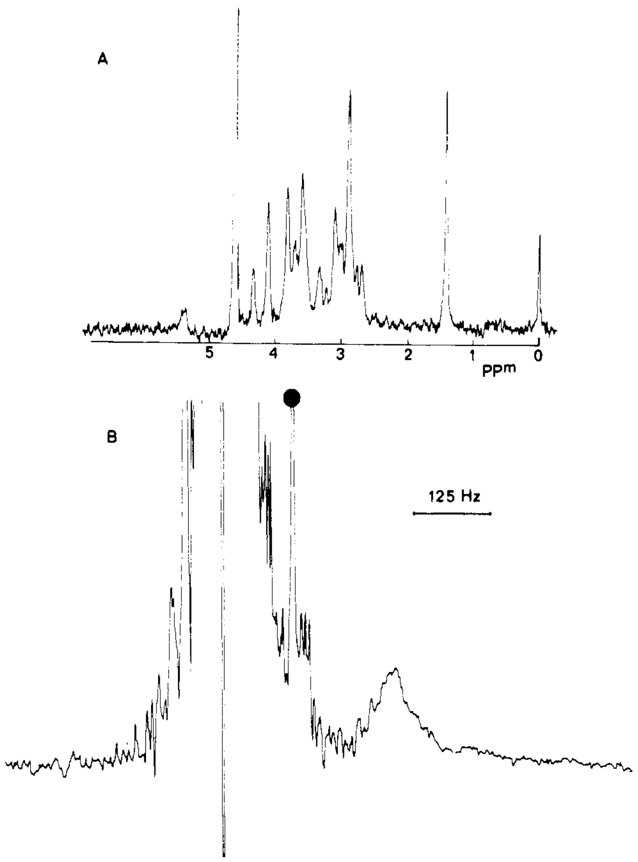

Figure 1. ^1H NMR spectra of (A) $[Co(azacapten)]^{3+}$ and (B) $[Co(azacapten)]^{2+}$ ions in D_2O solution (●, internal reference TMAT, 3.17 ppm).

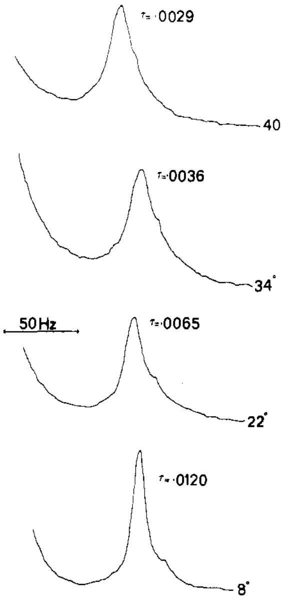

Figure 2. Exchange-broadened methyl resonance in a D_2O solution of $[Co(azacapten)]^{3+}$ and $[Co(azacapten)]^{2+}$ ($[Co^{2+}]$ = 0.012 M, $[Co^{3+}]$ = 0.024 M). τ (best fit line shape) is reported at each temperature.

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(9) $[Co(diamsarH_2)]^{4+}$ is the diprotonated form of the diamino-capped cage complex [(1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)cobalt(II)](4+).

Table I. Variation of the Chemical Shift and Line Width of the Methyl Resonance in $[Co(azacapten)]^{2+}$ with Temperature[a]

T, K	δ[b]	J, Hz	T, K	δ[b]	J, Hz
276.0	2.74	68.6	300.0	2.51	46.8
281.0	2.69	63.8	308.0	2.44	40.2
290.0	2.60	55.5	313.0	2.40	36.3

[a] The signal of the corresponding methyl group in $[Co(azacapten)]^{3+}$ is invariant with increasing temperature. [b] Chemical shifts were measured relative to the internal reference tetramethylammonium triflate (TMAT); however, in the Table the values are reported relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) (TMAT = 3.17 ppm).

of the methyl resonance in a mixture of solutions of the Co(III) and Co(II) complexes. This two-site exchange model has been employed previously for a number of fast exchange reactions involving complexes of iron,[10–14] ruthenium,[13] osmium,[13,14] manganese,[15,16] and mercury.[17]

A D_2O solution of the cobalt(II) and cobalt(III) complexes sealed in an NMR tube, under an inert atmosphere of O_2-free nitrogen, exhibited in the ^1H NMR spectrum at 3 °C a broadened CH_3 resonance, which when the temperature was raised to 40 °C broadened further (Figure 2). The resonance subsequently narrowed with further temperature increase. This behavior reflected both the paramagnetic narrowing of the cobalt(II) resonance with change in temperature and the transition to fast exchange on the NMR time scale.[18] The chemical shift differences and line widths in the absence of exchange were obtained from an ^1H NMR spectrum of the cobalt(II) species and are reported in Table I.

The study of the electron-transfer reactions was effectively limited to three concentration conditions by the surprising insolubility of the cobalt(II) complex and the time constraint for spectral accumulation. For the three sets of experiments the ionic strength varied between $\mu = 0.17$ M and $\mu = 0.29$ M.

For the two-site model, the second-order rate constant for electron self-exchange, k_2, was calculated from the difference between the natural line width of the pure diamagnetic species and the line width when a measured amount of paramagnetic species was present. The line width in the absence of exchange for the cobalt(III) sample was approximated at each temperature with use of the line width of an internal reference sample,[19] in this case tetramethylammonium triflate. In this way it was possible to estimate the cobalt(III) line width concurrently with the line-broadening measurements. The Binsch CLATUX computer program[20] was used to generate best fit line shapes for the exchange-broadened resonance using as input the chemical shifts, line widths, and mole fractions of paramagnetic and diamagnetic species present in solution. From the best fit line shape and the mole fraction of paramagnetic and diamagnetic species, τ_P and τ_D, the mean lifetimes for the paramagnetic and diamagnetic sites, respectively, were obtained. The first-order rate constants for exchange between the diamagnetic and paramagnetic sites were given by $k_{P\to D} = 1/\tau_P$ and $k_{D\to P} = 1/\tau_D$.[19] The analysis of data using this approach has been extensively described.[18–21]

Table II. Electron Self-Exchange Kinetic Data for $[Co(azacapten)]^{3+/2+}$

T, K	$10^{-2}k_2$, M^{-1} s^{-1}	T, K	$10^{-2}k_2$, M^{-1} s^{-1}	T, K	$10^{-2}k_2$, M^{-1} s^{-1}
$[Co^{2+}] = 0.012$ M, $[Co^{3+}] = 0.024$ M[a]					
276.0	20	295.5	42	360.8	76
281.5	23	300.5	55	313.0	95
289.5	32				
$[Co^{2+}] = 0.012$ M, $[Co^{3+}] = 0.036$ M					
276.3	17	295.0	38	308.0	65
281.8	23	301.8	49	315.0	91
288.0	31				
$[Co^{2+}] = 0.012$ M, $[Co^{3+}] = 0.017$ M					
281.0	20	304.0	59	313.0	95
292.5	31				

[a] $[Co^{2+}]$ = concentration of $[Co(azacapten)]^{2+}$; $[Co^{3+}]$ = concentration of $[Co(azacapten)]^{3+}$.

Variation in concentration of the reduced and oxidized forms of the cage complexes indicated that the system obeyed second-order kinetics overall with

$$\nu_{et} = k_2[Co(III)][Co(II)]$$

A plot of $1/\tau_P$ vs. [Co(III)] at 25 °C was linear, and the second-order rate constant, $k_2 = 4500$ (±300) M^{-1} s^{-1}, was evaluated from the slope with use of a linear least-squares analysis. The activation parameters for the self-exchange reaction were determined by a linear least-squares fit of the variable-temperature data, Table II, using a plot of ln k_2/T vs. $1/T$. The enthalpy and entropy of activation were $\Delta H^\ddagger = +7$ (±3) kcal mol^{-1} and $\Delta S^\ddagger = -18$ (±11) cal deg^{-1} mol^{-1}.

The activation parameters for the $[Co(azacapten)]^{2+/3+}$ self-exchange reaction appear typical of those observed for proposed outer-sphere processes; $\Delta H^\ddagger$ is low and $\Delta S^\ddagger$ negative.[22–26] For many outer-sphere reactions $\Delta H^\ddagger$ has been found to fall in the broad range 3–11 kcal mol^{-1}.[22–25] It has been suggested that the entropy term reflects the unfavorable entropic work required to bring together the large cationic components. It has also been determined that $\Delta S^\ddagger$ is insensitive to variations in ionic strength, such variations being reflected in $\Delta H^\ddagger$.[25,26]

The solid-state magnetic moments of the cobalt(II) hexaamine cage complexes are indicative of a high-spin $t_{2g}{}^5e_g{}^2$ configuration,[1,27] but for the $[Co(azacapten)]^{2+}$ complex the magnetic moment in the solid state and in solution is indicative of the low-spin $t_{2g}{}^6e_g{}^1$ configuration.[27] The solution moment is slightly higher than anticipated for $S = 1/2$. However, it is within the range observed for other low-spin octahedral cobalt(II) complexes.[28–37] Conceivably the difference could

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reflect a spin equilibrium in solution.[38,39]

The electron-transfer cross-reaction between [Co(azacapten)]$^{3+}$ and [Co(diamsarH$_2$)]$^{4+}$ was also measured, the latter being an encapsulated cobalt(II) complex with protonated amine groups on each cap.[2,9] With use of the experimentally determined self-exchange rates for electron transfer, k_{11} and k_{22}, for these cage complexes the rate of this electron-transfer cross-reaction, k_{12}, may be calculated from the Hush[40]–Marcus[41] theory, where

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

Here, K_{12} is the equilibrium constant for the electron-transfer reaction and f_{12} is a frequency factor (~ 1). From the standard reduction potentials for [Co(azacapten)]$^{3+/2+}$ and [Co(diamsarH$_2$)]$^{5+/4+}$, +0.01[42] and +0.06 V,[43] respectively, and the self-exchange rates 4500 and 0.024 M^{-1} s^{-1},[6] respectively, k_{12} is calculated to be 4.0 M^{-1} s^{-1}. The experimentally determined cross-reaction rate constant is 19 M^{-1} s^{-1}, in moderate agreement with that calculated. In general, the hexaamine cage complexes have been shown to fit the predictions of the Hush–Marcus theory for a number of cross-reactions.[6] The experiment therefore allows an independent estimate of the azacapten self-exchange rate that is consistent with the NMR result within the error of such correlations.

Discussion

Crystallographic investigations of the [Co^{III}azacapten]$^{3+}$ and [Co^{II}(azacapten)]$^{2+}$ ions show Co–N bond lengths of 2.01 and 2.07 Å, respectively, and Co–S bond lengths of 2.23 and 2.13 Å, respectively,[3,44] For the [Co(sep)]$^{3+/2+}$ ions the Co–N bond lengths are 1.99 and 2.16 Å, respectively.[1,2] The smaller Co(II)–N bond lengths for the azacapten vs. those of the sep complex are consistent with the low-spin condition in the former ion compared with the high-spin state of the latter. The slightly larger bond length observed for the Co(III)–N bond (2.01 Å) is also consistent with the somewhat smaller ligand field parameter deduced from the spectroscopic results for the Co(III) ion.[3]

The smaller ligand field parameters for the N$_3$S$_3$ chromophore compared with those for the hexaamine cages are consistent with the thioether component of the field. The low-spin condition of the Co(II) ion therefore presumably arises from a smaller interelectronic repulsion parameter generated by the sulfur atoms. A splitting was observed in the first ligand field band for the [Co^{II}(azacapten)]$^{2+}$ ion, which is consistent with the expectation from the Tanabe–Sugano diagram that the first spin-allowed transitions for a low-spin d^7 ion are of similar energy.[45] These bands can therefore be assigned as arising from transitions with $^2E \rightarrow {}^2T_1$ and $^2E \rightarrow {}^2T_2$ parentage in O_h symmetry.[45] A broad transition is also observed at approximately 780 nm in solution. This may arise from the $^2E \rightarrow {}^4T$ spin-forbidden transition.[45] Solid-state spectra of samples in the form of a KBr disk do not permit an unambiguous assignment of the origins of this band.[46]

The much faster self-exchange rate in Co(azacapten) compared to that in Co(sep) may be explained in terms of the smaller Franck–Condon barriers associated with the low-spin Co(azacapten)$^{2+}$. The low-spin condition is consistent with the reduced Co(II)–N bond length. For electron transfer, the complementarity of the spin states is therefore preserved and the Co(II)–N bond has to undergo a much smaller compression that for the Co(II) sep ion in order to reach the transition-state geometry. The electron-transfer rate constant is reminiscent of those for outer-sphere electron-transfer reactions of strong internal field strength ligands such as Co(terpy)$_2$$^{2+}$/Co(phen)$_2$$^{3+}$ and Co(terpy)$_2$$^{2+}$/Co(bpy)$_2$$^{3+}$, where k_{et} = 3.0 × 10^4 and 1.3 × 10^4 M^{-1} s^{-1}, respectively, at 25 °C.[47] Here the Co(II) terpyridyl complexes are known to be low spin in some lattices. All the complexes are at least close to the spin-crossover point, and the free energy differences between them are small.[47]

In a preliminary publication, the significance of steric strain in the cage complexes was explored to show how it could account for the electron-transfer rate differences between the Co(NH$_3$)$_6$$^{2+/3+}$, Co(en)$_3$$^{2+/3+}$, and Co(sep)$^{2+/3+}$ systems.[48] In these instances the Co–N distances are the same within each oxidation state and the magnetism and ligand fields are also very similar. The strain energy was found to be largely incorporated in bond angle and torsional deformations in the molecule. Such deformations are evident in the crystal structures of the Co(II) and Co(III) sep ions, a point also recognized by Geselowitz.[49] So far we have not developed the force field to account for the change from the N to the S atom donors in the present system, but clearly a substantial component of the increase in rate should come from the reduced need to compress the Co(II)–N bond length in the activated complex. A more detailed analysis of the relative contribution from this source must await the strain energy calculations on the azacapten ions. It suffices for the moment to say that the Co(II)–Co(III) electron-transfer rates in the amines and in the present system correlate at least qualitatively with the intramolecular reorganizational energies assessed by the strain calculations and the bond length changes involved.

The accelerating influence of thioether donor atoms on electron-transfer rates for cobalt(III) complexes has been noted previously.[50–55] The ability of the thioether atoms to stabilize the lower oxidation state and thereby facilitate electron transfer from the reductant has been suggested as the reason for the observed rate enhancement.[54] This notion is incorporated in the argument mentioned previously provided the stabilization is equated with reduced bond lengths and low-spin conditions for the Co(II) ions.

There is a possibility that the enhanced electron-exchange rate of the azacapten system relative to that for the sepulchrate ions arises from more overlap of the 3d orbitals of the sulfur atoms in the transition state relative to that for the hexaaza systems. The increased d-orbital extension of such systems relative to those of N could be a significant factor. Also there

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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.

Registry No. Co(azacapten)$^{3+}$, 81505-65-9; Co(azacapten)$^{2+}$, 86161-69-5; [Co(azacapten)](S_2O_6), 86161-70-8; [Co(azacapten)](CF_3SO_3)$_2$, 86161-71-9; [Co(diamsarH_2)]$^{4+}$, 85664-44-4.

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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_2Ph, 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

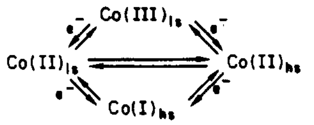
In a recent series of papers, we have been investigating the effect of spin state and spin equilibria on the redox reactions of iron(III) and iron(II) complexes.[1-4] In these studies we have shown that a relationship can sometimes be observed between the iron spin state and standard heterogeneous rates 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 $Co(II)_{hs\rightleftharpoons ls}/Co(I)_{hs}$ and $Co(II)_{hs\rightleftharpoons ls}/Co(III)_{ls}$ 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_2Ph. These complexes, whose general structure is shown in Figure 1, were earlier shown to exhibit a $^2E(ls) \rightleftarrows {}^4T(hs)$ 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_2Ph, were synthesized as previously reported.[5] Solvents utilized were methylene chloride (CH_2Cl_2), ethylene chloride ($EtCl_2$), acetone ($(CH_3)_2CO$), acetonitrile (CH_3CN), dimethylformamide (DMF), dimethylacetamide (DMA), butyronitrile (PrCN), benzonitrile (PhCN), pyridine, and dimethyl sulfoxide (Me_2SO) and were of reagent grade. Methylene chloride and ethylene chloride were distilled over P_2O_5. Acetone and acetonitrile were dried over molecular sieves and then distilled. All other solvents were dried and stored over 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.

Scheme I



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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