

Theory of adiabatic Hexammine-Co(III)-Self-Exchange

1. INTRODUCTION

The experimental rate determination and theoretical understanding of the 

\[
\text{[Cd(NH}_3}_3\text{]Cl}_2 \rightarrow \frac{1}{2} \text{[Cd(NH}_3}_3\text{]Cl}_2 + \frac{1}{2} \text{[Cd(NH}_3}_3\text{]Cl}_2
\]

reaction involving pieces of adsorbed gas and metal atoms has been a great intellectual challenge for several decades. Despite the substantial effort, the mechanism of the reaction is still an unsolved problem. The reaction mechanisms have been widely studied and various experimental results have been reported. However, the reaction is not well understood, and the rate constant is not well defined.

In this paper, we address the problem by considering the reaction between two adsorbed species, \([\text{Cd(NH}_3}_3\text{]Cl}_2\) and \([\text{Cd(NH}_3}_3\text{]Cl}_2\). The reaction is known to be thermally activated, and it is expected to be highly exothermic. The activation energy of the reaction is expected to be around 10 kJ/mol. The reaction is expected to be first-order in both reactants, and the rate constant is expected to be around 10^3 M^-1 s^-1.

However, the reaction is not well understood, and the rate constant is not well defined. Therefore, we propose a new approach to address the problem. We propose a new model that accounts for the effect of the adsorbed species on the reaction rate. The model is based on the assumption that the adsorbed species alter the reactivity of the reactants, and that the reaction rate is determined by the relative concentration of the adsorbed species.

In this model, the reaction rate is given by the following equation:

\[
\text{rate} = k \cdot [\text{reactant}] \cdot [\text{adsorbed species}]
\]

where \(k\) is the rate constant of the reaction and \([\text{adsorbed species}]\) is the concentration of the adsorbed species.

The model is expected to be more accurate than previous models, and it is expected to provide a better understanding of the reaction mechanism. The model is expected to be applicable to a wide range of reactions involving adsorbed species, and it is expected to provide new insights into the nature of the reaction process.

This model is expected to be tested experimentally, and the results are expected to provide new insights into the nature of the reaction process. The model is expected to be applicable to a wide range of reactions involving adsorbed species, and it is expected to provide new insights into the nature of the reaction process.
lations exploiting that DFT usually stabilizes high-spin over low-spin states. If Co(II) has a low-spin ground state, this would also explain why the optical absorption $^2E_g <^4T_{1g}$ has not been observed.

The paper is organized as follows. In section II we review further experimental and previous theoretical efforts in more detail. In section III we introduce the DFT code SIESTA and explain our computational methods (section IIIA), as well as present the calculation of the PESs (section IIIB). In section IV we provide a new estimate of the spin-allowed hexaamine self-exchange reaction based on our insights from the PESs and discuss our results. Finally, we summarize in section V.

II. REVIEW OF PREVIOUS EFFORTS

In this section further experimental facts about the single complexes and a more detailed review of past theoretical efforts are presented.

It is well accepted that $Co(NH_3)_5^{3+} [Co(III)]$ is a stable low-spin ($S=0$) compound, while it is assumed that $Co(NH_3)_5^{4+} [Co(II)]$ is high-spin ($S=3/2$). There are several reasons for this. First it is known from $^{15}N$ Co NMR studies that the related system, $Co(H_2O)_5^{3+}$, shows no sign of exchange with para-magnetic species[15] and hence is low-spin. This is also expected to be true for Co(III), since it has an even larger ligand-field favoring low-spin.

X-ray diffraction data of related crystals shows further a drastic difference of the Co-N bond distances ($\approx 0.22 \AA$ [5, 16]) between Co(II) and Co(III). From this it was concluded that the ligand-field of Co(II) must be much smaller resulting in high-spin. Additionally, the optical excitation spectrum of Co(III) could be fully characterized including $d-d$ spin-forbidden transitions. This is different than Co(II), where it could not be measured successfully. It is further experimentally supported that the $Co(NH_3)_5^{2+/3+}$ self-exchange reaction occurs as outer-sphere. This is due to a rather slow ligand exchange rate of Co(III). There is considerable thermodynamic and kinetic stability, which arises from effective $\sigma$-donation into empty $e_g$-shells[17].

The theoretical effort is conveniently discussed in the context of the separable semi-classical transition-state model[18]

$$k_{el} = K_{eq} \nu_{eff} \Lambda T \exp(-\beta G^t).$$

In this equation, $K_{eq}$ is the pre-equilibrium factor describing the probability to form a precursor compound, $\nu_{eff}$ is an effective nuclear attempt frequency to reach the transition state (TS), $\kappa_{el} < 1$ is the electronic transmission coefficient evaluated at the TS and averaged over all possible precursor compounds, $\Lambda > 1$ is the nuclear tunneling factor, and the Boltzmann factor (classical Franck-Condon factor) gives the probability to reach the TS with activation free-energy $G^t (\beta = 1/(k_B T))$. For the further discussion we review the nomenclature of the important states in figure 1, i.e. their group theoretical representations, total spin $S$, degeneracy $g$, and possible couplings (1) to (4). The couplings (1) and (3) are due to spin-orbit coupling or thermal population at finite temperature $T$, and (2) and (4) are mainly due to mixing of the electronic $e_g$-orbitals of Co(II) and Co(III) mediated by their ligands when a precursor state is formed.

It has been known for about 50 years that extraradial slow rates can often be attributed to small Franck-Condon nuclear overlaps. These originate from large changes in the metal-ligand bond length in the first coordination sphere[19]. This seemed to apply also to the case at hand, if one assumes an adiabatic reaction $k_{el} \approx 1$ "neglecting" the spin-forbiddeness. However, a first detailed theoretical study by E. Bullies and co-workers using perturbation theory in the weak spin-orbit coupling to admix spin-excited states shows that the electronic factor $k_{el}$ is very diabatic, $k_{el} \approx 10^{-4} [16]$. This makes the rate constant too small.

Orgel[20] and by Stynes and Ibers[21] put out an idea that the reaction could involve thermally excited Co(II, S=1/2) making it spin-allowed. Lasson et al[22] went further and argued that the excited states can become much lower in energy near TS. The important quantities are the energy difference between first excited state and ground state of Co(II) and Co(III) as a function of the Co-N bond length $r$

$$\Delta E^{2+/3+} (r) = E_r^{(2,3+)} - E_r^{(1,3+)}$$

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In the case of Co(III) the lowering enhances somewhat the admixture to the ground state, while in case of Co(II), $^2E_g$ becomes even lower than $^1A_g$ circumventing the spin-barrier. Their argument is based on Born-Oppenheimer potential energy surfaces (PES) calculated both with ab initio Hartree-Fock (HF) and semi-empirical INDO-CI methods including $\varepsilon_\gamma$ JT effects for both excited states. Unfortunately their result was not convincing, since the HF calculation predicts the wrong ground state for Co(III), while the INDO-CI excitation energy $\Delta E^{2+}$ was $2,000 - 3,000$ cm$^{-1}$ much lower than the generally believed $9,000$ cm$^{-1}$, although there is no experimental evidence for this value. There has been no absorption found in this region. On the other hand, the excitation energy of Co(III) is known from experiment to be $13,700$ cm$^{-1}$ at the Co(III) equilibrium configuration. Since their calculated value $\Delta E^{2+} = 14,800$ cm$^{-1}$ is too large by an amount $c \approx 1,100$ cm$^{-1}$, the PES from INDO-CI were corrected according to

\[
\Delta E^{3+} \rightarrow \Delta E^{3+} - c \\
\Delta E^{2+} \rightarrow \Delta E^{2+} + c.
\]

It was noted that the semi-empirical INDO-CI method is generally very successful in calculating spectra of transition-metal complexes at fixed geometries, but not so in predicting molecular geometries.[24]

In 1991, Newton carried out new ab initio calculations at both the SCF(UHF) and correlated (UMP2) level. Using an empirical correction factor as large as $c = -6,000$ cm$^{-1}$ (HF generally favors high-spin), he estimated the excitation energies at the transition state to be $\Delta E^{3+} = 8,800$ cm$^{-1}$ and $\Delta E^{2+} = 5,300$ cm$^{-1}$, and concluded that thermally excited pathways are not competitive to the spin-forbidden ground state pathway at room temperature (RT). This left the problem unsolved.

III. AB INITIO CALCULATIONS

A. Method

Our results of the inner-sphere activation barrier are based on PESs obtained from the fully ab initio code SIESTA[25] based on density functional theory (DFT). SIESTA uses Troullier-Martins norm-conserving pseudo potentials[26] in the Kohn-Sham Bylander form.[26]. For cobalt, we included spin-polarization and non-linear core corrections[27] to account for a spin-dependent exchange splitting and correlation effects between core and valence electrons, respectively. Relativistic effects are included for the core electrons in the usual scalar-relativistic approximation (mass-velocity and Darwin terms) and by averaging over spin-orbit coupling terms, while no spin-orbit coupling is included for the 4s and 3d valence electrons. This has the computational advantage that spin remains a good quantum number, while resulting errors of the total energy are less crucial when one is interested in total energy differences. SIESTA uses a local basis set of pseudo atomic orbitals (PAO) of multiple ζ-type. The first-ζ orbitals are produced by the method by Sankey and Niklewski[28], while the higher-ζ orbitals are obtained from the split valence method well known from quantum chemistry. Polarization orbitals can also be included. We used a double-ζ basis set with polarization orbitals (DZZ), as well as the generalized gradient approximation (GGA) in the version by Perdew, Burke and Ernzerhof[29] for the exchange-correlation energy functional. The charge densities are calculated on a real space grid, where the fineness of the grid corresponds to an energy cut-off 80 Ry.

Before going into the details of how we obtained the PESs plots, we outline the main ingredients of our calculations.

- Our calculations rest on the fixed-spin method within the spin-polarized DFT framework. Two different Fermi energies, one for spin-up and one for spin-down, are adjusted in a self-consistent way in order to obtain the ground state of a desired total spin. If a ground state of a certain spin is higher than the ground state of a different spin, then we know the former as the excited state and the latter as the true ground state. Nevertheless, there might be several states within a spin manifold which differ in orbital symmetry. Since the DFT method is based on the variational principle, we obtain the state of a system with a certain total spin which has the lowest energy[30]. Our excitation energies are extracted from total energy differences using the well-established self-consistent-field method (ΔSCF)[31]. This gives generally reliable results for molecules since final state effects are included.

- The ammines are treated as rigid bodies, i.e. the N-H bond lengths and the H-N-H bond angles stay the same throughout all our calculations. This is justified, since the vibrational frequencies of covalent bonds (N-H) are about one order of magnitude higher than the metal-ligand stretching frequencies[6] and are considered average values.

- We perform geometrical conjugate gradient optimizations (CGOs) of both Co(II) and Co(III) with the spin being fixed to a desired value. This is used to obtain the equilibrium geometries (EQ-GEOS) and the PES. The EQGEOS are optimized or relaxed geometries, where the forces on cobalt and all the ammines are below the chosen tolerance $0.01 \text{eV/Å}$. As far as the PESs calculations, we constrain the maximum size of a CG step to be $0.001 \text{Å}$ in order to provide a large sequence of energies. The resulting total energy can subsequently be plotted as a function of the Co-N bond length averaged over the six ligands. In the case of JT distortions, the average Co-N bond length in the axial
direction, $r_{eq}$, and the average Co-N bond length in the equatorial plane, $r_{eq}$, are more reasonable choices.

**B. Calculation of potential energy surfaces**

In the following we describe the procedure of how we obtained the PES plots in figures 2 and 3.

Figure 2 shows the ground state (S=0) and excited state (S=1) PESs of Co(III). For the ground state PES we started a CGO at the Co(II,S=3/2) EQGEO, denoted as starting point (1), but with the spin fixed to $S=0$ and charge $+2e$. For the excited state PES (S=1) we started CGOs at both the EQGEOs of Co(III,S=0), starting point (2), and Co(II,S=3/2) (not shown for clarity). The vertical arrow indicates the optical excitation energy from the Co(III,S=0) EQGEO, where it is assumed that the excited state is initially not JT distorted, since the excitation is almost instantaneous. The dotted line in figure 2 corresponds to total energy versus the average Co-N bond length. Since Co(III,S=1) is JT unstable, we also plot the total energy versus the average axial Co-N bond length, $r_{ax}$, and the average equatorial Co-N bond length, $r_{eq}$, shown by dashed lines. One can see that essentially only $r_{eq}$ changes when starting a CGO from the Co(III,S=0) EQGEO.

In order to obtain smooth PESs it is essential to treat the amines as rigid bodies. If one relaxes all the atoms, the resulting PES would be much more complicated, i.e. the PES would display a sequence of short parabolic curves stemming from periods of contracting or stretching the N-H bond lengths, or from changing the H-N-H angles. The resulting PES would not resemble smooth parabolic-like curves (at least for the non-JT distorted ground states) anymore, since the reaction coordinate would not simply be the change of the Co-N bond length. Although equilibrium energies of the constraint complexes might be higher than the all-atom-relaxed ones, this is not a problem, since we are interested in energy differences and finally in the sum of the Co(II) and Co(III) system energies (overall energy shift which does not affect the rate).

Figure 3 shows the ground state S=3/2 and excited state S=1/2 PESs of Co(II) as a function of the Co-N bond length averaged over all six ligands. Using an analogue procedure, the Co(II,S=3/2) PES results from a CGO starting at the Co(III,S=0) EQGEO, (1), where we have fixed the spin at $S=3/2$ and the charge at $+2e$. The dotted line shows the Co(II,S=1/2) PES, which was obtained from starting at the non-JT distorted Co(III,S=0) and Co(II,S=3/2) EQGEOs, (2) and (3) respectively. They stay non-JT distorted. The vertical arrow indicates the optical excitation to the non-JT distorted Co(II,S=1/2) state. Starting geometry (4) is JT distorted and hence lower in energy than (1). Further relaxation with the CGO method (dashed curve) lowers the energy drastically by up to 7.7 kcal/mol compared to the non-JT relaxed energy (dotted curve). The non-JT distorted PES (dotted curve) is hence only meta stable. The energy of the Co(II,S=1/2) EQGEO is only 0.3 kcal/mol (less than $k_BT$) higher than the Co(II,S=3/2) EQGEO.

Table I contains calculated equilibrium Co-N bond lengths of the ground and excited states and their experimental analogues. For comparison it also shows the one of the Co(H$_2$O)$_{5+3+}$ ground states. As typical for the DFT method they are overestimated, about 3% for NH$_3$ and 8% for H$_2$O ligands.
TABLE I: Equilibrium Co-ligand bond lengths for cobalt hexaammine and hexaaqua complexes in units of Å. Jahn-Teller (JT) distorted values: $r_{ax}$ denotes the Co-ligand bond length in axial direction, while $r_{eq}$ in the equatorial plane.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{1}A_g$</th>
<th>$^{2}E_g$</th>
<th>$^{3}T_{1g}$</th>
<th>$^{2}E_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NH$_3$)$_6^{3+}$</td>
<td>2.03</td>
<td>2.30</td>
<td>2.01</td>
<td>2.20</td>
</tr>
<tr>
<td>Co(NH$_3$)$_6^{2+}$</td>
<td>2.22</td>
<td>2.17</td>
<td>2.42</td>
<td>2.03</td>
</tr>
<tr>
<td>Co(H$_2$O)$_6^{3+}$</td>
<td>2.02</td>
<td>2.25</td>
<td>1.87</td>
<td>2.08-2.10</td>
</tr>
<tr>
<td>Co(H$_2$O)$_6^{2+}$</td>
<td>2.02</td>
<td>2.25</td>
<td>1.87</td>
<td>2.08-2.10</td>
</tr>
</tbody>
</table>

$^a$ From reference [44].

Table II compares theoretical and experimental optical excitation energies. The excitation energy $^{2}E_g \rightarrow ^{1}A_g$ for Co(NH$_3$)$_6^{3+}$ is not known from experiment but is very important. If this energy separation is low enough Co(II,S=1/2) is well-populated at ambient temperatures and the electron transfer reaction is spin-allowed. Although absolute excited state energies from DFT cannot be trusted, trends established from DFT are often correct. From table II we can obtain the following. Since DFT underestimates optical gaps such as the $^{2}E_g$ ligand-field, DFT favors high-spin compounds. For instance, the ligand-field splitting of Co(III) is 274 kJ/mol, while SIESTA gives 246 kJ/mol. In other words, excitations from low-spin to high-spin ($^{5}T_{1g} \rightarrow ^{1}A_g$) are underestimated while excitation from high-spin to low-spin ($^{2}E_g \rightarrow ^{1}A_g$) are overestimated. Similar results were found for singlet-triplet gaps of phenyl-nitrene and other hypervalent systems [36].

Unfortunately, in the case of low-spin to high-spin excitations there is only one reliable value for Co(III) and no experimental value available for Co(H$_2$O)$_6^{3+}$ in order to confirm the trend. Nevertheless, we can easily see that the calculated gap for Co(H$_2$O)$_6^{3+}$ (7, 150 cm$^{-1}$) has to be a lower bound analogously to Co(III). The argument is as follows. From ligand-field theory, the excitation energy $^{3}T_{1g} \rightarrow ^{1}A_g$ is additive in the ligand field $D_g$, which is about 20% larger for NH$_3$ compared to H$_2$O [22]. Taking a value $D_g = 274 kJ/mol$ for Co(III) [35] and 200 kJ/mol for Co(H$_2$O)$_6^{3+}$ [36], we can correct the excitation energy of Co(III), 13, 700 cm$^{-1}$, by the $D_g$ difference and obtain an approximate value for Co(H$_2$O)$_6^{3+}$, 7, 500 cm$^{-1}$. This is clearly higher than the calculated value 7, 150 cm$^{-1}$. Having this trend established we can conclude that the excitation $^{2}E_g \rightarrow ^{4}T_{1g}$ of Co(NH$_3$)$_6^{2+}$, 3, 680 cm$^{-1}$, is an upper bound on the real value.

A further confirmation of the quality of our excitation energy of Co(II) comes from the fact that our value is similar to Larson’s with INDO-CI (3, 100-4, 100 cm$^{-1}$ after applying correction Eq. (6) [22]). According to figure 3, the JT distorted Co(II,S=1/2) equilibrium energy is only slightly higher than the non-JT distorted Co(II,S=3/2) equilibrium energy. Since the S=1/2 PES are likely too high by a constant energy shift, Co(II,S=1/2) could be close to degenerate with Co(II,S=3/2) or even be the true ground state. Note that these considerations do not include multiplet-spitting due to spin-orbit coupling, as well as entropy effects on the energy ($\sim -TS = -k_{B}T\ln(g)$, where $g$ is the degeneracy of the multiplet).

TABLE II: Spin-forbidden transition energies in units of 10$^3$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>$^{3}T_{1g} \rightarrow ^{1}A_g$</th>
<th>Co(H$_2$O)$_6^{3+}$</th>
<th>Co(NH$_3$)$_6^{3+}$</th>
<th>low-spin to high-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>calc.</td>
<td>1.15</td>
<td>13.23</td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>($&gt; 1.89$)</td>
<td>13.70 [36]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$^{2}E_g \rightarrow ^{4}T_{1g}$</th>
<th>Co(H$_2$O)$_6^{3+}$</th>
<th>Co(NH$_3$)$_6^{3+}$</th>
<th>high-spin to low-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>calc.</td>
<td>8.40</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>exp.</td>
<td>14.24 [36]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^{4}$ From reference [44].

$^{5}$ The JT distorted Co(II,S=1/2) equilibrium energy is only slightly higher than the non-JT distorted Co(II,S=3/2) equilibrium energy. Since the S=1/2 PES are likely too high by a constant energy shift, Co(II,S=1/2) could be close to degenerate with Co(II,S=3/2) or even be the true ground state. Note that these considerations do not include multiplet-spitting due to spin-orbit coupling, as well as entropy effects on the energy ($\sim -TS = -k_{B}T\ln(g)$, where $g$ is the degeneracy of the multiplet).

TABLE III: Energy difference $\Delta E^{3/2+}(r)$ in units of 10$^3$ cm$^{-1}$ at the equilibrium position $r_{eq}(S)$ of Co(II,S=0) (Co(II,S=3/2)) and at the transition state $r_{t}$ of the conventional spin-forbidden process. The values of $r_{t}$ of this work, Larson’s, and Newton’s are 2.00, 2.03, and 2.14 Å respectively.

<table>
<thead>
<tr>
<th>$r_{t}$</th>
<th>Co(II,S=0)</th>
<th>Co(II,S=3/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{2}E_g \rightarrow ^{4}T_{1g}$</td>
<td>13.73</td>
<td>12.0</td>
</tr>
<tr>
<td>$^{3}E_g \rightarrow ^{5}T_{1g}$</td>
<td>3.41</td>
<td>1.19</td>
</tr>
</tbody>
</table>

$^{4}$DFT-GGA method.

$^{5}$INDO-CI method, empirically corrected energies by Eqs. (5,6) with $c = 1,100$ cm$^{-1}$, energy difference $\Delta E^{3/2+}$ is estimated from their Fig. 5

$^{6}$UMF2 method, empirically corrected energies by Eqs. (5,6) with $c = -6,000$ cm$^{-1}$.
energy difference at the spin-forbidden transition state. The excited state Co(III, S=1) is always much too high in energy to be relevant and is not important for further consideration. However, the value and sign (|ΔE2+(r)|) of the process will be spin-forbidden (allowed by weak spin-orbit coupling) if ΔE2+ > 0), or it is spin-allowed (ΔE2+ < 0).

The former process can be described by second order perturbation theory[6, 8, 12] using Co(II, S=1/2) as an excited state coupled to or at the spin-forbidden TS, the latter one is through direct coupling and does not involve spin-orbit coupling[22]. As one can see our value is ΔE2+(r+1) < 0 and hence the reaction along the lowest energy path is spin-allowed.

Figure 4 shows the PES of the total 2 Co-system, i.e. the sum of the single complex energies. The minimum in the left top corner at (rL = 2.03 Å, rR = 2.22 Å) corresponds to equilibrium CoL(III)CoR(II), where the subscripts L and R stand for “left” and “right”, respectively, and simply distinguish the two complexes. The minimum in the right bottom corner at (rL = 2.22 Å, rR = 2.03 Å) corresponds to equilibrium CoL(II)CoR(III). The variables rL and rR are the Co-N bond lengths of the left and right complex. For simplicity we can only show the non-JT distorted complexes, since a single JT distorted complex depends on two variables, r_a and r_b. This would resolve in a total potential which depends on more than two variables and cannot be plotted. Part A is plotted using the ground state Co(III, S=0) (solid line in Fig. 2) and Co(II, S=1/2) for Co(II)-N bond length r_2 < 2.125 Å (dotted line in Fig. 3) and Co(II, S=3/2) for r_2 > 2.125 Å (solid line in Fig. 3). This is an example (by not including JT distorted complexes of lower energy) of a spin-allowed reaction. However, if we restricted ourselves to the O_b group, this would be the lowest energy pathway. Such a reaction starts at equilibrium CoL(II, S = 3/2)CoR(III, S = 0), then activated by thermal fluctuations changes to the CoL(II, S = 1/2)CoR(III, S = 0) PES at (rL = 2.125 Å, rR = 2.03 Å) through spin-orbit coupling in only first order (presumably adiabatic). Coming back to figure 4, part B shows the PES of Co(II, S=0) and Co(II, S=3/2) and hence describes the conventional spin-allowed reaction with an energetically higher transition state.

In the following we have to obtain the activation barrier of the reaction. In figure 5 the transition states for spin-allowed (lower graph) and spin-forbidden (upper graph) are plotted. The graphs are the cross-section of the 2Co-PES from figures 4 A and B along the diagonal r := r_L = r_R, i.e. E(r_L = r, r_R = r) = E_{CoL(III)}(r) + E_{CoR(II)}(r), where the Co-N bond lengths r_L and r_R are the bond lengths of the “left” and “right” complex. The transition state is defined as the saddle point. Using non-JT distorted Co(II, S=1/2) leads to a lowering of the spin-forbidden transition state by 0.3 eV = 6.92 kcal/mol. The spin-allowed and spin-forbidden TSs are at r = 2.05 and 2.1 Å, respectively. In the next section we use the spin-allowed activation barrier to estimate the hexam-

![Figure 4: Contour plot of the PES of the total 2 Co-system with contour level spacing 0.03 eV = 0.06 kcal/mol. Only results from the non-JT distorted complexes are shown. A) Example of a spin-allowed reaction using Co(III, S=0) and non-JT distorted Co(II, S=1/2) for Co(II)-N bond lengths r_2 < 2.125 Å and Co(II, S=3/2) for r_2 > 2.125 Å (see Fig. 3). Within the O_b group this is the lowest energy reaction pathway. B) PES of conventional spin-forbidden reaction originating from Co(III, S=0) and Co(II, S=3/2).]
IV. RESULTS

In this section we give an estimate for the hexamine self-exchange rate using previously estimated electron transfer parameters and results from last section. For now, we take the energies obtained from the DFT calculations literally. For instance, we assume that high-spin Co(II, S=3/2) is the groundstate according to our calculation (see Fig. 3). However, since DFT stabilizes high-spin Co(II, S=3/2) over low-spin Co(II, S=1/2) according to our trend, this rate estimate is a lower bound. This is because we first have to thermally excite to the reaction intermediate, Co(II, S=1/2), which lowers the rate. With regard to our trend, Co(II, S=1/2) could be the true groundstate.

The initial rate constant to the intermediate state Co(II, S=1/2)Co(III, S=0) is denoted by $k_i$. In thermal equilibrium the return reaction with rate constant $k_{-i}$ back to the groundstate Co(II, S=3/2)Co(III, S=0) is equal to $k_i$. From the intermediate state the spin-allowed electron transfer can occur with rate constant $k_{et}$.

$$C_{et}(II, S = 3/2)C_{et}(III, S = 0) \xrightarrow{k_i}$$
$$C_{et}(II, S = 1/2)C_{et}(III, S = 0) \xrightarrow{k_{et}}$$
$$C_{et}(III, S = 0)C_{et}(II, S = 1/2) \xrightarrow{k_{et}}$$

The resulting total rate constant is $k$. Since the two steps from Eq. 7 are incoherent due to relaxation along the surfaces, the total rate $k$ can equivalently be described as starting out at the thermally populated (with probability P) intermediate, $C_{et}(II, S = 1/2)C_{et}(III, S = 0)$, from the spin-allowed electron transfer can occur to $C_{et}(III, S = 0)C_{et}(II, S = 1/2)$ with rate $k_{et}$. This does not require rate constant $k_i$. Hence, the total spin-allowed reaction rate constant is

$$k = P k_{et} = \underbrace{g e^{-\beta \Delta G^*}}_Z k_{et} \quad \quad \quad (8)$$

with $k_{et}$ being the electron transfer rate Eq. (2). The prefactor or probability P applies in the case that Co(II, S=1/2) is the excited state, which has first to be thermally populated. $\Delta G^* = \Delta E^* - T \Delta S$ is the free energy of excitation and Z is the partition function.

There are two main differences from previous rate estimates:

- Co(II, S=1/2) and Co(II, S=3/2) are nearly degenerate, i.e. Co(II, S=1/2) is slightly higher in energy than Co(II, S=3/2) but is probably overestimated.
- In order to get a lower bound of the rate we hypothetically trust the DFT energies and calculate $\Delta G^* = 0.3 k \text{cal/mol} + k_{et} \text{Trin}(12/4) = 3.1 \text{cal/mol}$.

The entropy differences between Co(II, S=1/2) and Co(II, S=3/2). Hence, the prefactor of equation (8) is 0.09 using the degeneracies $g$ from figure 1 and neglecting multiplet-splitting.

FIG. 5: Cross-section of 2Co-PES, written as E(total charge in roman letters, total spin); along $r_L = r_R$. The TS is defined as the saddle point. Using Co(II, S=0) and non-JT distorted Co(II, S=1/2) lowers the TS by 0.3kcal/precursor complex = 6.92kcal/mol compared to using Co(II, S=3/2) and Co(II, S=3/2) (arrow (1)). Arrows (2) and (3) indicate the two activation barriers being the difference between the energy at the transition state (superscript $i$) and at the EQGEO (superscript 0).
• The TS of the Co(II,S=1/2)/Co(III,S=0) system is lower than the TS of Co(II,S=3/2)/Co(III,S=0).

The inner-sphere contribution to the activation barrier, the energy difference of the 2 Co-system between the TS and equilibrium using Co(II,S=1/2), is only $E_{iv}^\ddagger = 0.42\text{eV} = 9.69\text{kcal/mol}$. For the equilibrium energy of Co(II,S=1/2), we take the JT distorted value, for TS we use the non-JT distorted one. This seems reasonable, because the acceptor, Co(III,S=0), is non-JT distorted. In order to have sufficient nuclear overlap, the donor should be non-JT distorted at TS, too.

The other parameters are only slightly modified. This is mainly due to using a different nuclear frequency for Co(II), i.e. $\nu_2(E^\ddagger)$ for Co(II,S=1/2) instead of $\nu_2(A_{1g})$ for Co(II,S=3/2):

The product $K_{equ,eff} = 1.4 \cdot 3 \cdot 10^{11}(M_s)^{-1}$ has been estimated before for the spin-forbidden process by Sutin [6] and Newton[8,10] using a pre-equilibrium constant $K_{equ} = 0.013M^{-1}$ and an effective nuclear frequency $\nu_{eff} = 347cm^{-1}$[8]. Since the case at hand is slightly different (low-spin Co(II,S=1/2)), we redefine $\nu_{eff}$. The average harmonic frequency is given by[6, 43, 44]

$$\nu_{eff} = \frac{\nu_{2solv}^2 E_{solv}^1 + \nu_{2in}^2 E_{in}^1}{E_{solv} + E_{in}}$$

where $\nu_{2solv} = \sqrt{\nu_2\nu_3} / \sqrt{\nu_2^2 + \nu_3^2}$ is the reduced inner-sphere nuclear frequency of Co(II) and Co(III). Using the experimental values $\nu_2(E^\ddagger) = 255cm^{-1}$ and $\nu_2(A_{1g}) = 494cm^{-1}$[11], respectively, we obtain $\nu_{in} = 320cm^{-1} = 9.6 \cdot 10^{12}s^{-1}$. For the solvent, we use a typical value $30cm^{-1} = 0.9 \cdot 10^{12}s^{-1}$[44]. We do not attempt to estimate $\nu_3$ from the PES due to complications from JT distortions in the case of Co(II,S=1/2). The outer sphere, $E_{solv}^1 = 28/4\text{kcal/mol} = 7\text{kcal/mol}$, was previously determined by Bulks and colleges applying the Marcus-Levich continuum model for the solvent[11, 12]. We neglect entropy contributions, which are quite small for water near room temperature[43] and vanish for the inner-sphere system, if the (harmonic) vibrations are the same for the activated complex and the reactants[6]. Using these parameters, one obtains $\nu_{eff} = 245cm^{-1} = 7.3 \cdot 10^{12}s^{-1}$ and $K_{equ,\nu_{eff}} = 0.5 \cdot 10^{12}(M_s)^{-1}$.

The electronic transmission coefficient for the $e_{g}$ transfer was determined by Larson and colleges to be weakly adiabatic, $\kappa_{el} \approx 0.5$[22], using parameters for the spin-forbidden process and standard Landau-Zener theory[45]. Extended Hückel theory was applied to calculate the donor(D)-acceptor(A) electronic coupling, $\tilde{B}_{DA} = \rho(D) [\tilde{H}_{DA}]$, for different precursor complexes (apex-to-apex, apex-to-edge, apex-to-side). A subsequent orientational averaging gave $\tilde{B}_{DA} \approx 200cm^{-1}$. Their statistical analyses assumes that each complex can rotate independently and that each configuration covers the same solid angle. The Co-Co separation was chosen $7\AA$ (van der Waals contact between first solvation shells), the Co-N distances of both complexes were fixed at $2.06\AA$ reasonably close to our TS value, $2.05\AA$. A similar procedure was applied by Newton[8]. Utilizing $\tilde{B}_{DA}$ from above, our parameters $E_{solv}^1, \nu_{in,eff}$ and Eqs. (7-11) from Ref.[8, 46], we redefine the electronic transmission and nuclear tunneling factors and obtain adiabaticity $\kappa_{el} = 0.73$ and weak nuclear tunneling $\Gamma_n = 1.9$, respectively.

Finally, the activation barrier has inner- and outer-sphere contributions and is lowered by the average electronic coupling at TS, i.e. $G^\ddagger = E_{solv}^1 + E_{in,eff}^1 - \tilde{B}_{DA}$, and is given by $G^\ddagger = 0.70\text{eV} = 16.0\text{kcal/mol}$. This leads to a Boltzmann factor $e^{-G^\ddagger} = 2.1 \cdot 10^{-12}$. Including all the calculated charge transfer parameters in Eq. (8) gives a rate constant of $6 \cdot 10^{-3}(M_s)^{-1}$ which is about 2 orders of magnitude larger than experiment. Possible sources of errors are discussed in section V.

In the following we again want to stress the main differences between our treatment of a spin-allowed process and the conventional spin-forbidden reaction by Bulks et al. and Newton[8]. The main difference is that in our case the low-spin Co(II,S=1/2) complex has a lower energy than the high-spin Co(II,S=3/2) near the TS as opposed to Bulks et al. and Newton. In their case, the spin excited state Co(II,S=1/2) is much higher in energy and is only virtually coupled to the weak spin-orbit coupling. This leads to extremely small rates of order $10^{-10}(M_s)^{-1}$. In Table III we show for further illustration the individual parameters used to calculate the rate according to Eqs. (2) and (8) and compare to Newton’s spin-forbidden and hence diabatic groundstate reaction and thermally excited adiabatic pathway. The spin-forbidden reaction is significantly lowered by the weak spin-orbit coupling ($\kappa_{el} \ll 1$), while the excited alternative is thermally not accessible and leads to even smaller rates. The $2E_g \leftrightarrow 4T_{2g}$ excitation energy is as large as 9, 100cm$^{-1}$, while in our case it is only 3, 680cm$^{-1}$.

V. DISCUSSION

At this point, there are two main possibilities why there is a 2 order of magnitude disagreement between our, $6 \cdot 10^{-3}(M_s)^{-1}$, and the experimental rate, $5 \cdot 10^{-3}(M_s)^{-1}$. Either something is not correct with the theoretical estimate, or the experimental rate constant is too small. In the more likely case that the theory misses some details, the sources of possible errors are the $2E_g \leftrightarrow 4T_{2g}$ excitation energy and hence the prefactor of Eq. (8). Increasing the energy of the Co(II,S=1/2) PESs w.r.t. Co(II,S=3/2) by a constant energy shift $2,560cm^{-1}$ and hence increasing the excitation energy to 6, 240cm$^{-1}$, produces the experimental value. This, however, is in conflict with the trend of excitation energies established from the DFT method.

Another vague possibility of errors in our theory could
TABLE IV: Rate parameters (see Eqs. (2) and (8)) used in this (spin-allowed) and Newton’s (spin-forbidden and thermally excited) work. The rates are compared with experimental estimates. (!) indicates main differences between Newton’s and our work[7,8].

<table>
<thead>
<tr>
<th>exp.[3, 4, 10]</th>
<th>this work</th>
<th>Newton[8]</th>
<th>thermally excited</th>
<th>spin-forbidden</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g/\hbar$</td>
<td>$k_{eq}$</td>
<td>$\nu_{eff}$ [cm$^{-1}$]</td>
<td>$\kappa_{el}$</td>
<td>$\Gamma_{\nu}$</td>
</tr>
<tr>
<td>0.28</td>
<td>0.013</td>
<td>245</td>
<td>0.73</td>
<td>1.9</td>
</tr>
<tr>
<td>0.013</td>
<td>0.013</td>
<td>347</td>
<td>$10^{-6}$ (!)$^d$</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$includes $\Delta G^\circ$ from Eq. (8)
$^b$individual parameters are presented to the best of our knowledge
$^c$due to a large $2E_g \sim 4T_1 \Delta$ excitation energy of 9, 100 cm$^{-1}$
$^d$due to a spin-orbit reduction factor of $\gamma^2 = 1.8 \cdot 10^{-4}$.

originate from a more complicated cross-over from the JT distorted Co(II, S=1/2) equilibrium complex to thermally excited non-JT distorted Co(II, S=1/2) near TS. The cross-over could be rather unlikely, since the symmetry changes.

On the other hand, possible experimental issues are beyond our realm of knowledge. Although a difficult experiment, it has been thoroughly studied over decades. Nevertheless, generally forgotten, neglected or underestimated side-reactions lead to an underestimation of the rate constant. In particular, the existence of high-spin Co(II, S=3/2) is challenged by our analysis. This leads to the question, if the assumption of high-spin Co(II, S=3/2) was wrongly made when deriving certain rates of side-reactions. Having said this, an error of about 2 orders of magnitude in the rate estimate is not as bad as it may sound. Due to the activated nature of the reaction, the exponential dependence of the rate on the activation barrier and excitation energy makes it very sensitive to small errors.

VI. CONCLUSION

Within Marcus theory of charge transfer the rate constant of the hexaamminecobalt self-exchange reaction was rederived. We utilized the DFT code SIESTA to calculate Born-Oppenheimer potential energy surfaces and spin-excitation energies and use previously determined parameters. The main differences from former work is the near degeneracy of Co(II, S=3/2) and Co(II, S=1/2). Furthermore, we observed a drastic lowering of the activation barrier (\( \sim 6.9 \text{ kcal/mol} \)) for the reaction pathway involving and Co(III, S=0) and Co(II, S=1/2). This led to a rate constant of order \( 6 \cdot 10^{-5} (\text{M s}^{-1}) \), which is 2 orders of magnitude faster than experiment. Possible sources of errors are outlined in section V and having most likely to do with the neglect of the proper cross-over treatment from Jahn-Teller distorted equilibrium Co(II, S=1/2) to non-Jahn-Teller distorted Co(II, S=1/2) near the transition state. The good quality of our energetics involved in the rate constant evaluation is indicated, first because our calculated excitation energy 13, 230 cm$^{-1}$ of Co(III), $^3T_{1g} \leftrightarrow ^1A_g$, agrees well with the experimental value 13, 700 cm$^{-1}$. Second, our excitation energy 3, 860 cm$^{-1}$ of Co(II), $^2E_g \leftrightarrow ^2T_{1g}$, is close to Larsson’s value from INDO-CI (3, 100 - 4, 100 cm$^{-1}$). This energy is in particular important for charge transfer. Unfortunately, the corresponding optical absorption peak could not be found experimentally. This may simply be explained by the spin-forbiddenness and vibrational broadening because of differences in equilibrium Co-N bond distances and a Jahn-Teller unstable excited state. On the other hand, our analysis questions the existence of the high-spin ground state Co(II, S=3/2) and hence can provide an alternative explanation for the absence of the absorption peak.

Acknowledgement. We would like to thank P. Ordejón, E. Artacho, D. Sánchez-Portal and J. M. Soler for providing us with their ab initio code SIESTA. This work at Davis was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Research, and also received support from NSF IGERT "Nanomaterials in the Environment, Agriculture, and Technology".

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[46] Eq. 10 of Ref. [8] misses a factor $\left(h\omega_{cut}\right)^{-1}$. 