reaction mixture was maintained at 0 °C (3 days) and room temperature (9 days). Removal of volatile materials at −17 to −23 °C left behind a clear colorless liquid, which was 2.900 mmol of $C_6F_6[(CF_3)_3CO]_2Cl_2$ [yield 96%; bp 79–80 °C (2mm)].

The infrared spectrum of the liquid had the following bands ($cm^{-1}$): 1740 (w), 1341 (ms), 1264 (s), 1228 (ms), 1204 (ms), 1134 (s), 1093 (m), 1075 (m), 1033 (w), 989 (s), 972 (s), 914 (w), 899 (w), 837 (m), 744 (m), 730 (s), 708 (w), 690 (w), 542 (w).

The $^{19}F$ NMR spectrum contained a very strong band at $\phi$ −71.6 and additional multiplets in the $\phi$ −115 to −157 region. The mass spectrum for $C_6F_6[CF_3)_3CO]_2Cl_2$ had the following *m/e* peaks: 707, 709, 711, $(M - F)^+$; 691, 693, $(M - Cl)^+$; 637, $(M - Cl_2F)^+$; 491, 493, 495, $[M - (t\text{-}R_fO)]^+$; 456, 458, $[M - (t\text{-}R_fO) - Cl]^+$; 437, 439, $[M - (t\text{-}R_fO) - ClF]^+$; 425, 427, $[M - (t\text{-}R_fO)\text{–}CFCl]^+$; 421, $[M - (t\text{-}R_fO) - Cl_2]^+$; 394, 396, $[t\text{-}R_fO(CF)_4Cl]^+$; 285, $(C_{10}F_7O_2)^+$; 237, 239, $(C_6F_6ClO)^+$; 235, $(t\text{-}R_fO)^+$; 225, 227, $(C_5F_5ClO)^+$; 221, 223, $(C_6F_6Cl)^+$; 219, $[(CF_3)_3C]^+$; 211, 213, $(C_7F_4ClO)^+$; 209, 211, $(C_5F_6Cl)^+$; 209, $(C_5F_7O)^+$; 202, $(C_6F_6O)^+$; 197, $(C_4F_7O)^+$; 187, 189, $(C_5F_4ClO)^+$; 186, $(C_6F_6)^+$; 175, 177, $(C_4F_4ClO)^+$; 171, 173, $(C_5F_4Cl)^+$; 159, 161, $(C_4F_4Cl)^+$; 155, $(C_5F_5)^+$; 147, $(C_3F_5O)^+$; 131, $(C_3F_5)^+$; 124, $(C_4F_4)^+$; 117, 119, 121, $(CFCl_2O)^+$; 117, $(C_5F_3)^+$; 113, 115, $(C_2F_2OCl)^+$; 109, $(C_3F_2Cl)^+$; 97, $(CF_3CO)^+$; 93, $(C_3F_3)^+$; 85, 87, $(CF_2Cl)^+$; 78, $(CF_2CO)^+$; 69, $(CF_3)^+$.

Anal. Calcd for $C_{14}Cl_2F_{24}O_2$: C, 23.13; F, 62.72; Cl, 9.75. Found: C, 24.40; F, 63.70; Cl, 10.25.

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**Registry No.** $(CF_3)_3COCl$, 27579-40-4; $CF_3I$, 2314-97-8; $I(CF_2)_2I$, 354-65-4; $SF_5(CF_2)_2I$, 51480-07-0; $C_6F_5I$, 827-15-6; $C_6F_6$, 392-56-3; $CF_3I[OC(CF_3)_3]_2$, 103067-96-5; $[(CF_3)_3CO]_2ICF_2CF_2I[(CF_3)_3CO]_2$, 103025-27-0; $SF_5(CF_2)_2I[OC(CF_3)_3]_2$, 103025-28-1; $C_6F_5I[(CF_3)_3CO]$, 103025-29-2; $C_6F_5I[(CF_3)_3CO]_4Cl_2$, 103025-31-6; $C_6F_6[(CF_3)_3CO]_2Cl_2$, 103004-24-6.

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# Hexaamminecobalt Electron-Self-Exchange Reaction

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The $Co(NH_3)_6^{2+/3+}$ electron-transfer reaction is reexamined. Using a semiempirical INDO method, we calculated the $^2E$ excited state of $Co(NH_3)_6^{2+}$ to be lower than previous estimates for the equilibrium geometry. For shorter metal–ligand distances the $^2E$ state appears to be the ground state. The lowest energy path for electron transfer is via the $^2E$ state, and this path is spin-allowed contrary to the ground state ($^4T_1$) to ground state ($^1A_1$) path. We also carried out calculations on the binuclear complex $[Co(NH_3)_6]_2^{5+}$ and found that the electron transfer is almost adiabatic. Our calculation of the thermal barrier naturally has large error bars, but we may conclude that there is now no apparent discrepancy between theory and experiment for the rate of $Co(NH_3)_6^{2+/3+}$ self-exchange.

## I. Introduction

The electron-exchange reaction between $Co(NH_3)_6^{3+}$ ($^1A_1$) and $Co(NH_3)_6^{2+}$ ($^4T_1$) has attracted considerable attention due to the spin transfer that accompanies the electron transfer.[1-4] According to the most recent experimental results[3,4] the rate of the reaction is $10^{-6}$–$10^{-5}$ $M^{-1}$ $s^{-1}$. This low rate can be satisfactorily explained as due to the large difference in Co–N bond length for the two oxidation states,[3,4] without any regard to the spin-forbidden character of the reaction. Buhks, Bixon, Jortner, and Navon examined the latter problem in detail[2] and found that the spin forbiddeness contributes a factor $\Delta_s = 2 \times 10^{-4}$ (dimensionless) to the rate constant. The reaction is thus far from being completely spin forbidden, but since the most recent experimental results apparently do not give room for any electronic nonadiabaticity, there is disagreement between theory and experiment.

A small spin factor $\Delta_s$ may be compensated to some extent by a large spatial factor $\Delta_r$ (dimension energy). The electronic factor $\kappa$ is obtained by the Landau–Zener approximation as[5,6]

$$\kappa = \frac{2P_0}{1 + P_0} \tag{1}$$

where

$$P_0 = 1 - \exp[-(\Delta_s\Delta_r)^2/\Delta_0^2] \tag{2}$$

$\Delta_0$ may be calculated to be $10^{-3}$ au for typical metal complexes at room temperature.[7] Buhks et al.[2] did not calculate $\Delta_r$ since they compared the ratio of exchange rates between the $Co(NH_3)_6^{2+/3+}$ and $Ru(NH_3)_6^{2+/3+}$ complexes. $\Delta_r$ can be expected to be the same for these two cases, and $\Delta_r$ then cancels out in the nonadiabatic theory,[2] where $\kappa$ is proportional to $(\Delta_r\Delta_s)^2$. However, if eq 2 is used, there would still be the possibility that $(\Delta_r\Delta_s)^2$ is sufficiently large to make $P_0$ approach unity and thereby offset $\Delta_s^2$ partly. The calculation of $\Delta_r$ (as described below in section II) showed that $\Delta_r$ is close to $10^{-3}$ au as for other pairs of metal complexes examined earlier.[8,9] Thus the problem with the small spin factor remains.

In several papers preceding the one by Buhks et al.,[2] it was assumed that the normal ground state to ground state reaction path was strictly spin forbidden and that the reaction had to proceed via the $^2E$ excited state of $Co(NH_3)_6^{2+}$ or the $^3T_1$ excited state of $Co(NH_3)_6^{3+}$. Buhks et al. showed that the ground state to ground state reaction is allowed by spin–orbit mixing.[2] They also made it appear likely that this path was energetically advantageous compared to the spin-preequilibrium mechanisms via either of the excited states using the argument that the excitation energy to the $^2E$ was as much as 9000 $cm^{-1}$. An objection to this

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argument is that electron transfer does not take place at the equilibrium geometry but at a much smaller Co–N distance, where the energy splitting is less according to the Tanabe–Sugano diagrams. Besides this, it appears that there is no hard evidence to support an excitation energy of 9000 cm$^{-1}$ as we discuss below.

Since the correct positions of the energy surface of the $^2$E state of $Co(NH_3)_6^{2+}$ and the $^3T_1$ surface of $Co(NH_3)_6^{3+}$ are crucial for an understanding of the electron-transfer mechanism, we decided to calculate the energy spectra for $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ using quantum chemical methods. Unrestricted and restricted Hartree–Fock ab initio self-consistent field (SCF) calculations gave equilibrium geometries with Co–N distances consistently too large by about 4% in cases where comparison to experiments can be made. Since the description of the high-spin states is favored in the Hartree–Fock approximation, the energy splitting between the spin states is incorrectly reproduced. To solve this problem within the ab initio framework requires extensive configuration interaction, including basis function of f type on Co, d type on N, and p type on H, and is still beyond reach on modern computers. We therefore decided to further investigate this problem using a semiempirical INDO–CI method developed by one of us.[10,11] This method has proven successful in separating the different spin states of transition-metal complexes. The result is that the $^4T_1$ state of $Co(NH_3)_6^{2+}$ crosses over into the $^2$E state before we reach the compressed geometry corresponding to the transition state. The electron transfer apparently occurs via a spin-preequilibrium mechanism, and is completely adiabatic. The barrier is about the same as obtained for the ground state to ground state transfer.

## II. Electronic Nonadiabaticity

Buhks et al.[2] wrote the ground-state wave function for the metal ions as

$$(Co^{3+})(Co^{2+}) = [{}^1A_1(t_2^6) + c_1\ {}^3T_1(t_2^5e^1)][{}^4T_1(t_2^5e^2)(J = 1/2)] \quad (3)$$

This wave function contributes $1.45 \times 10^{-4}$ to $\Delta_s^2$. The other two wave functions with $J = 3/2$ and $J = 5/2$ for the $^4T_1$ state mix with the $^2$E state, are thermally populated, and contribute to a total $\Delta_s^2 = 4 \times 10^{-4}$. In all cases the transfer occurs via e* orbitals. $\Delta_r$ is thus obtained as an orbital energy difference in a transition-state conformation where the relevant orbitals are of the type

$$[e^*(1) + e^*(2)]/2^{1/2} \qquad [e^*(1) - e^*(2)]/2^{1/2} \quad (4)$$

In the symmetric case, this conformation is obtained if all Co–N distances are equal. In the unsymmetric case, small modifications of the nuclear positions are necessary to obtain orbitals localized equally on each metal ion as in eq 4.

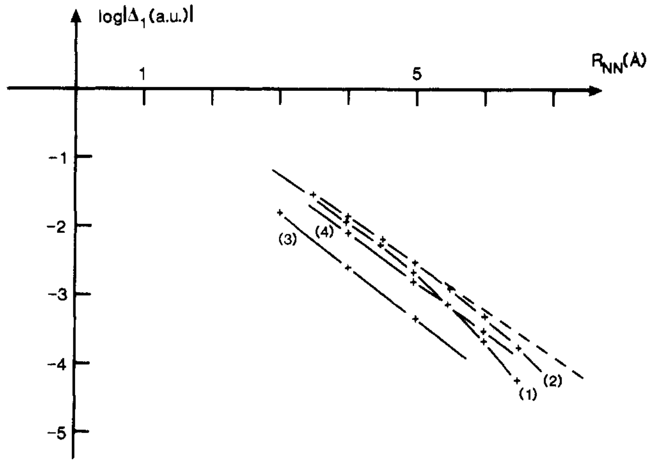

**Figure 1.** Calculated orbital energy differences between $\chi_1 + \chi_2$ and $\chi_1 - \chi_2$, where $\chi_1$ and $\chi_2$ are $NH_3$ lone-pair orbitals in the system $NH_3$–$H_3N$ with eclipsed geometry. The distance between the nitrogen atoms, *R*(N–N), is varied. (1) and (2) refer to ab initio Hartree-Fock calculations using basis sets 1 and 2, respectively. Basis set 1 for N:(9s5p) contracted to (3s2p) H:(4s) contracted to (1s).[13] In basis set 2 the basis for hydrogen is changed to (9s) contracted to (3s).[14] (3) is obtained in extended Hückel calculations using the parameters of ref 12 and (4) is obtained in calculations using the parameters of ref 15 for N(2p).

**Table I.** Calculated Values of $\Delta_r$ for Different Relative Orientations of the Two Complexes with Weights due to Abundancy[a]

| geometry | 169 × wt | $10^3\Delta_r$,[b] au | geometry | 169 × wt | $10^3\Delta_r$,[b] au |
|---|---|---|---|---|---|
| A–A | 9 | 8.89 | E–E$^\perp$ | 16 | 0.08 |
| A–E | 36 | 0.63 | E–S | 48 | 0.27 |
| A–S | 24 | 0.60 | S–S | 16 | 0.20 |
| E–E | 20 | 1.16 | | | av 0.93 |

[a] Key: A = apex; E = edge, S = side. *R*(Co–N) = 2.06 Å. [b] 1 au = 220 000 cm$^{-1}$; Co–Co = 7 Å.

In order to study the directional dependence of Δ, we carried out extended Hückel (EH) calculations.[12] The angular behavior of Δ should be rather accurately calculated by EH since it is due to phases and nodal surfaces of overlapping orbitals. One should rely less on the radial behavior since among other things this depends on the approximation of atomic orbitals. To reduce the error we compared EH to ab initio calculations on the system $NH_3$–$H_3N$ with the hydrogens pointing toward each other in an eclipsed fashion. $\Delta_r$ is obtained as the orbital energy difference between $\chi_1 + \chi_2$ and $\chi_1 - \chi_2$ where $\chi_1$ and $\chi_2$ are the N lone-pair orbitals. In Figure 1 the result is compared to the result of EH calculations. Basis set 1 is the same one[13,14] used for $Co(NH_3)_6^{2+}$ (see below). As we see, $\Delta_1$ decays faster than exponentially for increasing distance *R*(N–N). Since this was suspected to be due to the Gaussian basis set we also used an improved basis (basis set 2) for the hydrogen atoms: H (9/3). The behavior was now closer to exponential (Figure 1). The extended Hückel (EH) orbital energy differences between the + and − lone pair orbitals of $NH_3 \cdot H_3N$ are smaller than the ab initio results if the simple Slater orbitals are used. However, use of double-*Z* orbitals for N(2p)[15] (by Clementi and Roetti) improves the agreement with the ab initio results considerably (Figure 1). We therefore used the latter orbitals for N(2p) and similar double-*Z* orbitals for Co(3d) in the EH calculations on $[Co(NH_3)_6]_2^{5+}$. The difference in orbital energy between e and $t_2$ orbitals by the EH method for this choice of orbitals is 12 260 cm$^{-1}$ for *R*(CoN) = 2.16 Å and 21 000 cm$^{-1}$ for *R*(CoN) = 1.96 Å. These numbers are in reasonable agreement with the 10*Dq* values for $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ respectively.

In both complexes the Co–N distances were fixed at 2.06 Å in an octahedral geometry with a Co–Co distance of 7.0 Å. The octahedra are connected apex to apex (A–A), apex to edge (A–E), apex to side (A–S), etc. If each complex is rotated independently, assuming each configuration to cover the same solid angle, there appear a number of possibilities distributed on typical configurations as in Table I. $\Delta_r$ appears to be of the order $10^{-2}$ au (2200 cm$^{-1}$) for the A–A approach. The average $\Delta_r$ is $10^{-3}$ au for the 7-Å values of Table I. However, all conformations, except A–A, permit a closest Co–Co distance somewhat shorter than 7 Å, increasing the average $\Delta_r$. Therefore most conformations may be regarded as adiabatic ($\Delta_r > 10^{-3}$ au). On the other hand, conformations with the degenerate e* orbital occupied, directed othogonal to the Co–Co axis, also contribute with the same statistical weight (or slightly less because of slightly less stabilization energy) as the e* orbitals, but all these conformations have a negligible $\Delta_r$. To sum up, the spatial nonadibaticity factor seems to be as large as 0.5. Only the seldomly realized A–A conformations have a $\Delta_r$ large enough to be of importance in partly offsetting a small $\Delta_s$.

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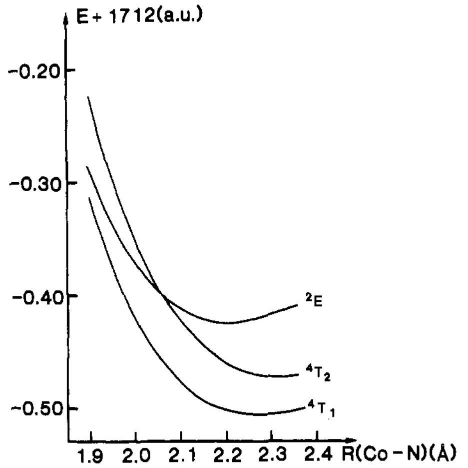

**Figure 2.** Results of ab initio Hartree–Fock calculations on $Co(NH_3)_6^{2+}$ using Gaussian basis sets.[13,18]

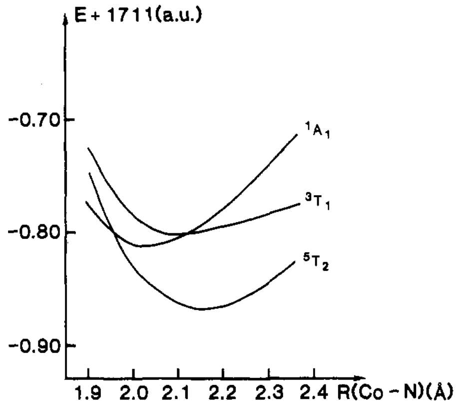

**Figure 3.** Results of ab initio Hartree–Fock calculations on $Co(NH_3)_6^{3+}$ using Gaussian basis sets.[13,18]

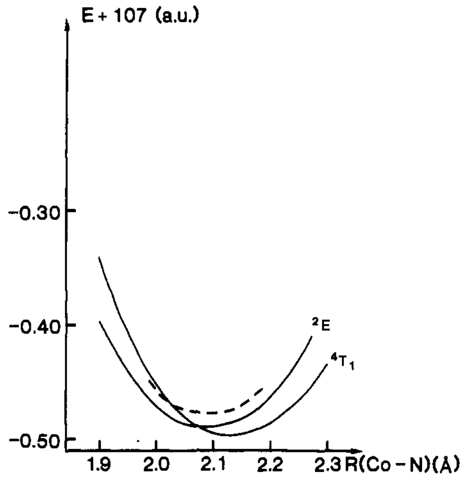

**Figure 4.** Results of INDO calculations on $Co(NH_3)_6^{2+}$. The broken line represents the corrected $^2E$ surface as described in the text.

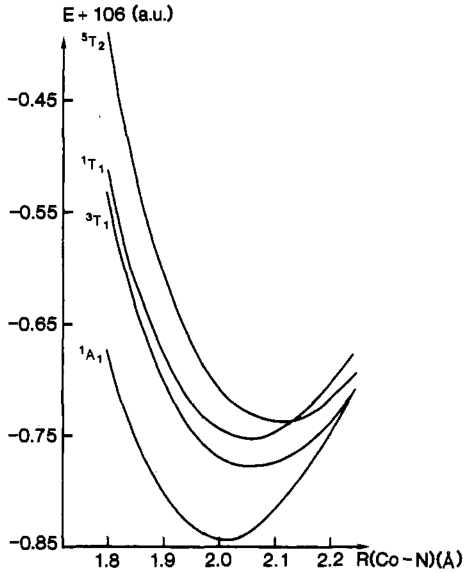

**Figure 5.** Results of INDO calculations on $Co(NH_3)_6^{3+}$.

## III. Ab Initio Calculations

Available ab initio programs[16,17] based on a Gaussian basis set were used. For Co we used a basis set[18] where each atomic orbital (1s, 2s, 2p, etc.) is expanded in three Gaussians, except the Co(3d) function, where four Gaussians are used, contracted to 3 + 1. The results are given in Figures 2 and 3. Unfortunately the results are in disagreement with experiments. For $Co(NH_3)_6^{3+}$ the ground state is predicted to be $^5T_2$ in obvious disagreement with experiment,[19] and for $Co(NH_3)_6^{2+}$ the excitation energy to the $^2E$ state is much higher than expected from crystal field theory.[20,21] The calculated equilibrium distances (Å) are 2.27 ($^4T_1$), 2.20 ($^2E$), and 2.32 ($^4T_2$) for $Co(NH_3)_6^{2+}$ and 2.03 ($^1A_1$), 2.16 ($^5T_2$), and 2.08 ($^3T_1$) for $Co(NH_3)_6^{3+}$. These distances are about 4% larger than the crystallographic distances in the ground states.[4,22] Expressed in ligand field terms the ab initio Hartree–Fock method seems to underestimate 10*Dq* and overestimate the electronic repulsion integrals *B* and *C*. This is in fact consistent with some results obtained earlier on similar systems[23,24] and with the general behavior of the Hartree–Fock approximation to give an energy advantage to the high-spin states.

The calculations show in any case that the energy gap between $^4T_1$ and $^2E$ decreases for a decreased Co–N distance. This is consistent with the crystal field expression for this energy difference in the strong-field coupling case

$$E(^2E) - E(^4T_1) = \text{const} - 10Dq \qquad (5)$$

where the constant is almost independent of 10*Dq*. 10*Dq* is about 10 000 cm$^{-1}$ [for $Co(NH_3)_6^{2+}$] at R = 2.16 but about 23 000 cm$^{-1}$ [for $Co(NH_3)_6^{3+}$] at R = 1.96. If the Hartree–Fock method underestimates 10*Dq* by a factor of 1.5 as has often been found[23] there is the possibility for intersection at $R$ = 2.0–2.1 Å.

The $^2E$ state may be expected to distort axially to a $D_{4h}$ conformation. We estimate from the Hartree–Fock calculations that the equilibrium $^2E$ geometry is $R$(Co–N) = 2.32 Å for the axial ligands and 2.14 Å for the equatorial ligands. The energy minimum is quite shallow, about 2000 cm$^{-1}$ below the octahedral one at $R$(Co–N) = 2.20 Å. The $O_h$–$D_{4h}$ symmetry descent thus leads to some stabilization of the supposed preequilibrium state at rather moderate geometrical distortions.

## IV. INDO Calculations

Ab initio calculations of the Hartree–Fock type are known to favor high multiplicities, as, for example, demonstrated in Figures 2 and 3. Configuration interaction (CI) corrects for this shortcoming, but such calculations we deemed to be impractical for systems of the size we are examining here. A rough estimate is that SCF favors open shells by 0.04 au per unpaired electron.[25] Applying this rule of thumb places the $^2E(t_2^6e^1)$ state of $Co(NH_3)^{2+}$ nearly degenerate with $^4T_1(t_2^5e^2)$, and reduces the energy of the $^1A_1(t_2^6)$ state of $Co(NH_3)_6^{3+}$ in such a fashion as to lie lowest in energy, followed by $^3T_1(t_2^5e)$ and $^3T_2(t_2^4e^2)$. These ex-

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**Table II.** Calculated Spectrum of $Co(NH_3)_6^{2+}$ at $R$ = 2.14 Å (the Calculated Minimum for Energy)

| state[a] | calcd, $10^3$ cm$^{-1}$ |  | exptl,[b] $10^3$ cm$^{-1}$ |
|---|---|---|---|
|  | $^2E$ as ref | $^4T_1$ as ref |  |
| $^4T_1$ | ... | ... | ... |
| $^2E$ | 2.0 | 2.9 |  |
| $^4T_2$[a] | 9.3 | 8.8 | 9.0 |
| $^4T_1$ | 18.1 | 17.5 | 18.5 |
| $^4A_2$ | 21.0 | 19.7 | 21.1 |

[a] Only quartet states are given. There are a number of doublet states calculated above the $^2T_1$ state at 11 000 cm$^{-1}$. [b] Reference 21.

**Table III.** Calculated Spectrum of $Co(NH_3)_6^{3+}$ at $R$ = 2.02 Å (the Estimated Minimum of Energy)

| state | calcd, $10^3$ cm$^{-1}$ | exptl,[b] $10^3$ cm$^{-1}$ | state | calcd, $10^3$ cm$^{-1}$ | exptl,[b] $10^3$ cm$^{-1}$ |
|---|---|---|---|---|---|
| $^1A_1$ |  |  | $^3T_1$ | 14.8 | 13.0 |
| $^1T_1$ | 20.3 | 21.0 | $^3T_2$ | 18.5 | 17.2 |
| $^1T_2$ | 27.3 | 29.5 |  |  |  |

[a] Reference 19.

trapolations based on experience with the failures of the ab initio SCF method are in accord with experiment.

In order to get a firmer idea of the relation between the $^4T_1$ and $^2E$ states of $Co(NH_3)_6^{2+}$ we performed SCF–CI calculations of the INDO/S type.[10,11,25,26] This methodology has been very successful in calculating the spectra of transition-metal complexes at fixed geometries, although less successful in calculating molecular geometries directly. The results from these calculations are summarized in Figures 4 and 5. The calculated equilibrium distances are 2.14 ($^4T_1$) and 2.09 Å ($^2E$) for $Co(NH_3)_6^{2+}$ and 2.02 ($^1A_1$), 2.06 ($^3T_1$), 2.07 ($^1T_1$), and 2.12 Å ($^5T_2$) for $Co(NH_3)_6^{3+}$. Figure 4 suggests that the $^4T_1$ and $^2E$ states cross at 2.07 Å but that the minimum of the $^2E$ state lies higher in energy than the minimum of the $^4T_1$ state.

The reference state curves are obtained from an SCF–CI on the $^2E$ or $^1A_1$ reference states of $Co(NH_3)_6^{2+}$ or $Co(NH_3)_6^{3+}$, respectively, by using the standard parameterization (calculated two-electron-repulsion integrals).[10] Energy differences between states are calculated by using the spectroscopic parameterization (empirical two-electron integrals).[26] The results, however, seem relatively insensitive to this choice, as demonstrated, for example, in Table II in which both the $^2E$ and $^4T_1$ states have been used as the reference state. The observed quartet spectrum of the Co(II) complex is reasonably well reproduced (Table II). The $^2E$ state is predicted to lie well below the estimated 9000 cm$^{-1}$ used by Buhks et al.[2] The calculated value of 2000–3000 cm$^{-1}$ may be low, but is not unreasonably so when comparing with the weaker field (thus favoring the quartet) hexaaqua complex with an crystal field derived[27] and calculated[11] $^4T_1 \rightarrow {}^2E$ transition energy of 9000 cm$^{-1}$. The fact that no absorption has been found in this region may be explained as due to the spin forbiddeness and vibrational broadening because of differences in equilibrium distances. Normally spin-forbidden transitions are seen only if there is small vibrational broadening.

Table III presents the calculated spectrum of $Co(NH_3)_6^{3+}$ at the calculated minimum of the $^1A_1$ reference state. In this case, the transition energies of the triplet states have been reported and examined in some detail.[17,33] The general shapes of these calculated curves (Figure 5) are similar to those that might be inferred from ligand field theory[20,21] and those reported by Wilson and Solomon[19] based on the observed spectrum. Although we have not examined the $^5T_2$ state in any detail, we calculate it to lie *above* the $^1T_1$ state until about 2.14 Å (0.12 Å from $R_e$ of the $^1A_1$ state).[17] The calculated values of the triplet states for the Co(III) complex are 1300–1800 cm$^{-1}$ higher than the observed values. Assuming this correction for the Co(II) complex leads to a corrected estimate for the important $^4T_1 \rightarrow {}^2E$ transition energy of 3300–4700 cm$^{-1}$. If it is assumed that the shapes of the curves of Figure 4 do not change, this leads to a crossing of the two curves at 2.04 Å (the broken line of the figure), close to the 2.02-Å value estimated for the activated state for direct transfer;[1] see below.

## V. Discussion

According to the calculation of Buhks et al.,[2] only the $J = {}^3/_2$ and $J = {}^5/_2$ components of the $^4T_1$ state with thermal populations of 34% and 7%, respectively, interact with the $^2E$ state. The interaction matrix elements are 230 and 691 cm$^{-1}$, respectively. These numbers are large enough to provide adiabatic crossing from the $^4T_1$ ($J = {}^3/_2$) and $^4T_1$ ($J = {}^5/_2$) states to the $^2E$ state.

The Co–N distance for the $^1A_1$–$^4T_1$ activated state is

$$R^{\ddagger} = \frac{k_{II}R_{II} + k_{III}R_{III}}{k_{II} + k_{III}} = 2.03 \text{ Å} \tag{6}$$

$k_{II}$ and $k_{III}$ are the vibrational force constants for the Co–N stretching frequencies ($k_{II}$ = 1.27 mdyn/Å; $k_{III}$ = 2.45 mdyn/Å[3,28]) and $R_{II}$ = 2.16 Å and $R_{III}$ = 1.96 Å are the equilibrium distances[3,22] of the two complexes. Figure 4 shows that at the distance $R^{\ddagger}$ = 2.03 Å, the $^2E$ state is lower than the $^4T_1$ state, and thus the barrier cannot be higher for the $^2E$ path. Unfortunately the situation is more complicated than this since, as pointed out above, the $^2E$ state is Jahn–Teller unstable and distorts axially. Although one might argue that the reaction path has $A_1$ symmetry, since it starts out on the (almost) symmetric $^4T_1$ energy surface, we will examine the energy barrier for the distorted reaction path.

Due to the symmetry of the self-exchange process the inner-sphere reorganization barrier may be written as

$$\begin{aligned} E_{in}^{\ddagger} = {} & 2 \times {}^1\!/_2 k_{III}(R_{III} - R_{ax}^{\ddagger})^2 + 4 \times {}^1\!/_2 k_{III}(R_{III} - R_{eq}^{\ddagger})^2 + \\ & 2 \times {}^1\!/_2 k_{II}(R_{II,ax} - R_{ax}^{\ddagger})^2 + 4 \times {}^1\!/_2 k_{II}(R_{II,eq} - R_{eq}^{\ddagger})^2 \end{aligned} \tag{7}$$

where $R_{II,ax}$, $R_{II,eq}$ and $R_{ax}^{\ddagger}$, $R_{eq}^{\ddagger}$ are axial and equatorial Co–N distances in the energy minimum of the excited $^2E$ state of $Co(NH_3)_6^{2+}$ and in the activated state, respectively. For the minimum energy path we obtain

$$R_{ax}^{\ddagger} = \frac{k_{III}R_{III} + k_{II}R_{II,ax}}{k_{III} + k_{II}} \qquad R_{eq}^{\ddagger} = \frac{k_{III}R_{III} + k_{II}R_{II,eq}}{k_{III} + k_{II}} \tag{8}$$

by requiring the partial derivatives of $E_{in}^{\ddagger}$ to be zero. We may assume that the Hartree–Fock method is reasonably accurate in predicting the distortion. We also found that the calculated equilibrium distances were uniformly too large by 4%. The assumption $R_{II,ax}$ = 2.22 Å and $R_{II,eq}$ = 2.04 Å is then consistent with the Hartree–Fock results since $R_{II,ax} - R_{II,eq}$ = 0.18 Å and the average $^1/_6(2R_{II,ax} + 4R_{II,eq})$ = 2.10 Å is 0.06 Å shorter than the experimental Co–N distance in $Co(NH_3)_6^{2+}$. We obtain from eq 8 $R_{ax}^{\ddagger}$ = 2.05 Å and $R_{eq}^{\ddagger}$ = 1.99 Å. From eq 6 we obtain $E_{in}^{\ddagger}(^2E)$ = 9.7 kcal M$^{-1}$ and $E_{in}^{\ddagger}(^4T)$ = 14.4 kcal M$^{-1}$. To $E_{in}^{\ddagger}(^2E)$ has to be added the energy difference between the minima of the $^2E$ and $^4T$ states. As seen in Figure 4, remembering the stabilization energy due to distortion of about 2000 cm$^{-1}$, we find that the latter energy difference should be between 0 and 6 kcal M$^{-1}$. We conclude that the thermal barrier is about the same as the $^4T_1$ barrier. With all calculational and experimental error bars in mind, a strict statement would be that we have found no evidence that the $^2E$ thermal barrier is higher than the $^4T_1$ barrier.

$Co(H_2O)_6^{2+/3+}$ exchange is known to have a larger rate constant than expected for direct exchange.[4,29] In this case either preequilibrium or inner-sphere mechanisms have been suggested[29,30]. Direct electron exchange between the ground states would have a spin factor $\approx 10^{-4}$ just as in the case of $Co(NH_3)_6^{2+/3+}$. High-spin states are at a lower energy for $Co(H_2O)_6$ than for $Co(NH_3)_6$ complexes.[21] For $NH_3$ ligands, 10*Dq* is in general 25% higher than for $H_2O$ ligands whereas for $F^-$ ligands it is 10% lower.[21] In accord with this $Co(NH_3)_6^{3+}$ and $Co(H_2O)_6^{3+}$ have low-spin ground states whereas $CoF_6^{3-}$ has a high-spin ground state. The

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excited $^5T_1$ for $Co(H_2O)_6^{3+}$ should therefore be close to the $^1A_1$ ground state in energy. The analysis of Winkler et al.[31] as well as much earlier considerations by Friedman et al.[32] suggest that the energy difference is only about 4 kcal mol$^{-1}$ with a rather much larger equilibrium distance for the $^5T_1$ state. The latter result is in agreement with spectroscopic results[19] as well as our calculations for $Co(NH_3)_6^{3+}$. Thus the $^5T_1$ state has an equilibrium bond length that is much closer to the one for the ground state of the Co(II) complex. This suggests a possible electron-transfer path via the $^5T_1$ or $^3T_1$ state for $Co(H_2O)_6^{2+/3+}$.[33] In the case of $Co(NH_3)_6^{3+}$ the $^5T_1$ is too high in energy,[19] however, to be of any importance as a preequilibrium state for electron transfer.

## VI. Conclusions

Electron exchange between $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$ in their respective ground states is spin forbidden in the absence of spin–orbit coupling. We suggest that the $^2E$ state for $Co(NH_3)_6^{2+}$ is closer in energy to the ground state ($^4T_1$) than believed previously. This suggestion is supported by INDO calcuations. In fact for small metal–ligand distances there is a crossing between the $^2E$ and $^4T_1$ energy surfaces. Thus for Co–N distances appropriate for electron transfer, the $^2E$ state is below the $^4T_1$ state. Due to spin–orbit coupling the $^4T_1$ states pass adiabatically to the $^2E$ state. Electron exchange between the $^2E$ state of $Co(NH_3)_6^{2+}$ and the $^1A_1$ state of $Co(NH_3)_6^{3+}$ is spin-allowed. The attempt was made to estimate whether the electron transfer between the two complexes, held close to each other in various conformations, was also spatially adiabatic. As for $Fe(H_2O)_6^{2+/3+}$, we found that $Co(NH_3)_6^{2+}/^{3+}$ was close to the border to nonadiabatic electron transfer.

The $^2E$ intermediate state, according to our calculations with all Co–N distances equal, lowers the thermal barrier for electron transfer somewhat. Since Jahn–Teller distortion of the $^2E$ state takes place, the barrier is again increased. Our calculations suggest, however, that the $^2E$ barrier is still lower than or is about the same as the $^4T_1$ barrier. This is in agreement with experimental results.[3,4]

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# Mechanisms of Ligand-to-Metal Intramolecular Electron Transfer in Cobalt(III)–Amine Complexes Containing a Coordinated Radical[1]

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The one-electron reduction of Co(III) complexes containing nitrophenyl ligands possessing differing lead-in and bridging groups by radiolytically generated $^\bullet CO_2^-$ and $^\bullet C(CH_3)_2OH$ radicals in neutral and acidic aqueous solution results in the formation of coordinated nitrophenyl ligand radicals. The UV–visible absorption spectra, the acid–base properties, and the decay kinetics of the transient intermediates were examined by pulse radiolysis. In neutral solution, the coordinated ligand radicals decay via intramolecular electron transfer from the coordinated nitrophenyl radical donor to the Co(III) acceptor. The values of the intramolecular electron-transfer rate constants depend on the isomeric position of the nitro group on the phenyl moiety, the structure of the bridging molecule between the redox sites, and the nature of the lead-in group to the metal center. Bridging structures between the initial radical site and the metal center of varying length, flexibility, and $\pi$-conjugation are incorporated into the 18 complexes studied. Correlation of the values of $\Delta H^*$ and $\Delta S^*$ of electron transfer with the structural relationship of the donor and acceptor sites leads to the proposition that four different mechanisms of intramolecular electron transfer operate in these complexes: through chain, direct and indirect ligand bypass, and nonadiabatic transfer. Protonation of the coordinated nitro radical greatly diminishes the rate of intramolecular electron transfer in the nitrophenyl carboxylato complexes; in most cases, protonation affects only the driving force for electron transfer while leaving the mechanism unchanged.

## Introduction

The study of the rates and mechanisms of electron-transfer reactions is fundamental to the understanding of many important biological redox sequences, including the respiratory chain and photosynthesis.[2] At the basis of these biological processes is the controlled sequential transfer of electrons between protein molecules that contain specific redox-active sites. Beyond its biological relevance, the understanding of the mechanisms of electron transfer between separated donor and acceptor sites has application to redox processes on electrode surfaces and to the reactivity of intermediates in homogeneous and heterogeneous catalysis. When the donor and acceptor sites are on a single molecule, electron transfer can occur intramolecularly without the kinetic influences of reactant diffusion and precursor substitution. These intramolecular systems, based conceptually on early developments by Taube,[3] model the "precursor complex" that precedes electron transfer in bimolecular redox reactions.[4]

The relationship between the rate of intramolecular electron transfer (IET) and the distance between the donor and acceptor sites has been examined by a number of investigators with a particular focus on long-range reactivity.[5-13] The relationship

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