Ligand-field Spectra of Cobalt(II) Ammines and Hexaamminecobalt(III/II) Electron Self-exchange

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Abstract

The energies of the ^2E state in hexaamminecobalt(II) and related complexes are estimated, and implications for the electron self-exchange reactions are discussed. Solution spectra of $[Co(NH_3)_6]^{2+}$ and $[Co(en)_3]^{2+}$ are presented, and analysis of these and related spectra permits confident assignment of the energies of the $^4T_{1g}$, $^2T_{1g}$, $^2T_{2g}$, $^2T_{1g}$ and $^4T_{1g}$ states. A ligand-field treatment leads to an estimate of the energy of the spectroscopic ^2E state in $[Co(NH_3)_6]^{2+}$ at approximately 6800 cm^{-1} above the ground state. For the $^2E/^1A$ pathway to have reorganizational energy close to that of the ground-state pathway, the octahedral ^2E state would have to have a minimum-energy bond length of 2.08 Å. It is concluded that the ^2E pathway probably lies near or slightly above the ^4T pathway in activation energy, and that the two paths cannot be readily distinguished.

Introduction

The question of the adiabaticity of electron transfer reactions has received a great deal of attention recently [1–5]. At issue is whether the transmission coefficient of a given reaction at its classical activated complex has a value of unity (adiabatic) or less than unity (non-adiabatic). The great success of the Marcus theory of electron transfer [6] in predicting the rates of a wide variety of electron transfer reactions suggests that most bimolecular electron transfer reactions are adiabatic, since the non-unity transmission coefficient of a non-adiabatic reaction would make its rate constant less predictable. However, there is considerable disagreement on this point.

One reaction in particular is notable in that it has often been considered a key example of non-adiabatic reactions: the electron self-exchange reaction of the hexaamminecobalt(III/II) couple

$$[Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+} \rightleftharpoons$$

$$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$$
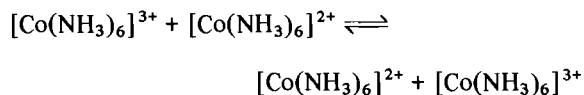
The chronology of the study of this reaction up to 1982 has been reviewed [7, 8]. It was proposed in 1956 that the electron self-exchange of this couple would be slow due to the 'spin-forbiddenness' of the reaction [9]. This idea was expanded upon by Buhks *et al.* [10] who concluded that the reaction was not totally spin-forbidden, but partially allowed by spin–orbit coupling, so that the transmission coefficient was approximately 10^{-4}. The rate constant was predicted to be approximately 10^{-9} M^{-1} s^{-1}, although this value would now probably have to be revised downward, since the authors based their calculation on a value of the Co(II)–N bond length of 2.114 Å, which is now known to be 2.18 Å [8, 11, 12].

However, an experimental measurement of the rate constant for the hexaamminecobalt electron self-exchange reaction has been performed [13] which shows that the rate constant of the reaction is approximately 8×10^{-6} M^{-1} s^{-1} at 40 °C. This value is consistent with the rate constant predicted by Marcus theory as well as by comparisons to similar complexes [7, 8, 12, 14]. It is apparent that, in fact, this electron transfer reaction has a transmission coefficient comparable to that of the [Ru(NH_3)_6]^{3+/2+} electron self-exchange reaction, which is generally assumed to be adiabatic. The [Co(NH_3)_6]^{3+/2+} electron self-exchange is thus most likely an adiabatic or nearly adiabatic reaction.

Recently, Larsson *et al.* [15] have attempted to explain the adiabaticity of the hexaamminecobalt electron exchange reaction by the interesting hypothesis, originally proposed by Stynes and Ibers [16], that the cobalt(II) partner as it is being compressed toward the activated complex crosses to the ^2E state which undergoes spin-allowed adiabatic electron transfer with the Co(III) partner. This hypothesis attempts to explain the adiabaticity of the electron transfer reaction while it leaves intact the assumption that the ground state ^4T plus ^1A reaction is strongly non-adiabatic. The authors estimate the energy of the $^2E/^1A$ pathway based on INDO calculations which place the spectroscopic ^2E state at 3300–4700 cm^{-1}, considerably lower than previous estimates. They conclude that the

$^2E/^1A$ pathway is within 0 to 25 kJ/mol of the $^4T/^1A$ pathway.

The difference in activation energy of the two pathways is an important value. If the paths are within about 5 kJ/mol, then it is unlikely that they could be distinguished experimentally, and the question of adiabaticity becomes moot. If the pathways are well separated, then experimental evidence can come to bear on the question. The purpose of the present communication is to review the evidence for the energy of the ^2E state in light of the ligand-field spectrum of the hexaamminecobalt(II) ion. We reexamine the solution spectra of $[Co(NH_3)_6]^{2+}$ and $[Co(en)_3]^{2+}$, analyze these spectra by comparison to other spectral data on these and related complexes, and reconsider the accessibility of the ^2E pathway.

Experimental

UV—Vis spectra were obtained on solutions in 1-cm quartz cells using a Hewlett-Packard 8452A spectrophotometer. Near-IR spectra were obtained on a Cary 14 spectrophotometer. Spectra of the appropriate solvents were used as references.

$[Co(NH_3)_6]^{2+}$

A solution 1.0 M in ammonium chloride and approximately 16 M in ammonium hydroxide (15.0 ml) and a solution 0.500 M in cobaltous chloride (5.00 ml) were deaerated by nitrogen bubbling, then mixed and transferred by cannula into a serum-capped cuvette, and the spectrum obtained.

$[Co(en)_3]^{2+}$

A solution of ethylenediamine dihydrochloride was neutralized with NaOH to give a solution 0.70 M in ethylenediamine and 0.30 M in ethylenediamine hydrochloride. This solution (7.50 ml) and 2.50 ml of a solution 0.205 M in cobaltous chloride were deaerated and mixed, and the resulting solution loaded by cannula into a serum-capped cuvette, and the spectrum obtained.

Results

The UV—Vis spectrum between 14 000 and 30 000 cm^{-1} of $[Co(NH_3)_6]^{2+}$ in solution is shown in Fig. 1, and summarized along with the NIR data in Table 1. Under the conditions used, Co(II) is approximately 87% in the form of the hexaammine and 13% in the aquapentaammine form, based on the stability constants of Bjerrum [17]. The spectrum consists of a NIR band at 9350 cm^{-1}, and a sharp shoulder at 18 800 cm^{-1} on the main visible absorption at $\nu_{max} = 20\,500$ cm^{-1}. The main band is asymmetrical around the maximum, being broader on the high energy side. No other absorption is apparent until 32 000 cm^{-1}.

The UV—Vis spectrum between 14 000 and 30 000 cm^{-1} of $[Co(en)_3]^{2+}$ in solution is shown in Fig. 2, and summarized in Table 2. The NIR band is found at 9900 cm^{-1}. A weak band is visible at 15 500 cm^{-1}. A sharp maximum at 18 800 appears as a side peak on the main band with maximum at 20 700 cm^{-1}. This main band is asymmetrical around the maximum with a possible shoulder at 21 700 cm^{-1}, and appears to have a smaller half-width than the corresponding band for $[Co(NH_3)_6]^{2+}$. No other absorption is observed on the high-energy side until about 37 000 cm^{-1}.
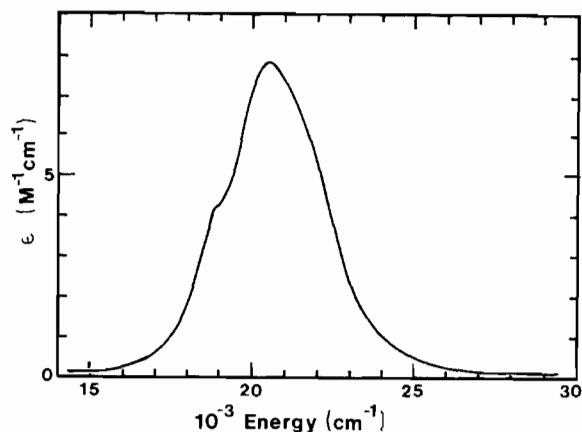

Fig. 1. Absorption spectrum of 0.125 M cobaltous chloride in aqueous 12 M ammonia/0.75 M ammonium chloride.

TABLE 1. UV—Vis absorption spectral data for $[Co(NH_3)_6]^{2+}$

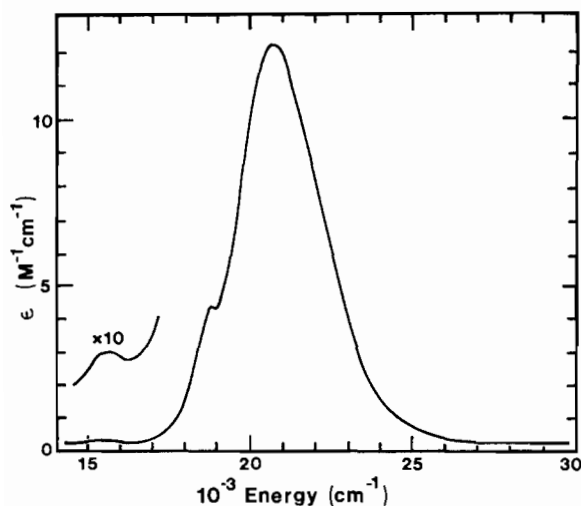| E [a] (cm^{-1})	ϵ (M^{-1} cm^{-1})	E [b] (cm^{-1})	ϵ (M^{-1} cm^{-1})	E [c] (cm^{-1})	ϵ (M^{-1} cm^{-1})
9350	2.5	9000	2.5	d	
sh 18800	4.3	sh 18500	4.0	sh 18800	6.0
20500	7.8	21100	8.0	20400	8.0
32300	0.5	d		d	

[a]This work.　[b]Ref. 18.　[c]Ref. 19.　[d]Not studied.

Fig. 2. Absorption spectrum of 0.0513 M cobaltous chloride in aqueous 0.53 M ethylenediamine/0.23 M ethylenediamine hydrochloride.

Discussion

Assignment of Spectral Data

The spectra presented here are in qualitative agreement with the previously published solution and crystal spectra for these ions, summarized in Tables 1 and 2, although there is a slight discrepancy between the values of the energies of the main peaks in the spectra of the two ions measured here and those given in the early work of Ballhausen and Jørgensen [18]. Also, it is apparent that the tailing UV absorption they reported above 25 000 cm^{-1}, not seen here, was due to the formation of the μ-peroxo-bridged species by adventitious air. Interestingly, the weak 15 500 cm^{-1} absorption band of [Co(en)$_3$]$^{2+}$, although not tabulated, is evident in their presented spectra. In addition to these spectra, the literature absorption and CD spectra of [Co(sep)]$^{2+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane), a cage complex with secondary amine ligands, are summarized in Table 3.

TABLE 3. Absorption and circular dichroism spectral data for [Co(sep)]$^{2+}$ [a]

E (cm^{-1})	ϵ (M^{-1} cm^{-1})	E (cm^{-1})	$\Delta\epsilon$ (M^{-1} cm^{-1})
10990	4.94		
15060	0.01	14800	−0.015
		15820	−0.024
18120	1.76		
18350	1.97	18350	−0.249
18550	1.87	19010	−0.205
		20400	−0.482
21400	8.21	22200	−0.258

[a]Λ-complex, ref. 21.

The spectra of [Co(NH$_3$)$_6$]$^{2+}$, [Co(en)$_3$]$^{2+}$ and [Co(sep)]$^{2+}$ can be seen to be strikingly similar. Using this similarity and the peak assignments for [Co(en)$_3$]$^{2+}$ by Yang and Palmer [20], based on room and low-temperature absorption spectra of [Co(en)$_3$](NO$_3$)$_2$ and CD spectra of cobalt-doped, spontaneously resolved [Zn(en)$_3$](NO$_3$)$_2$, the major bands can be assigned.

Reviewing Yang and Palmer's assignments, the low energy band of [Co(en)$_3$]$^{2+}$ is assigned to the $^4T_{2g}$(F) ← $^4T_1$ transition (using O_h symmetry states), in general agreement with other assignments. They assign CD absorptions at 15 300, 16 300 and 18 800 cm^{-1} to the $^2T_{1g}$(G), $^2T_{2g}$(G) and $^2T_{1g}$(P) transitions, as suggested by ligand-field theory and confirmed by the sharpness and vibronic progression of the bands, expected for the intraconfigurational transitions. The manifold at 20 900 cm^{-1} is primarily assigned to the $^4T_{1g}$(P), which is actually split slightly in the trigonal field. The $^4A_{2g}$(F) (t^{3}e^4) transition, predicted to be at about 21 700 cm^{-1}, is not observed. It is formally a two-electron transition and should be weak and broad, and it presumably underlies the $^4T_{1g}$(P) manifold.

The bands in the spectra of [Co(NH$_3$)$_6$]$^{2+}$ and [Co(sep)]$^{2+}$ are now easily assigned by com-

TABLE 2. UV–Vis absorption and circular dichroism spectral data for [Co(en)$_3$]$^{2+}$

E [a] (cm^{-1})	ϵ (M^{-1} cm^{-1})	E [b] (cm^{-1})	ϵ (M^{-1} cm^{-1})	E [c] (cm^{-1})	ϵ (M^{-1} cm^{-1})	E [d] (cm^{-1})	$\Delta\epsilon$ (M^{-1} cm^{-1})
9900	4.3	9800	5.0	10000	4.0	10000	−1.9
15500	0.3	15500[e]	≃0.5	[f]		15300	−0.01
[f]		[f]		[f]		16300	−0.01
18800	4.3	18700	5.0	18800	4.0	18800	−0.8
20700	12.1	21700	13.0	20900	9.4	20620	−1.8
21700	sh(?)			21700			

[a]This work.   [b]Ref. 18.   [c]Solid [Co(en)$_3$](NO$_3$)$_2$, ref. 20.   [d]CD of cobalt-doped [Zn(en)$_3$](NO$_3$)$_2$, ref. 20.   [e]Based on ref. 15, Fig. 1.   [f]Not observed.

parison to $[Co(en)_3]^{2+}$. Interestingly, $[Co(sep)]^{2+}$ not only plainly shows the $^2T_{1g}(G)$, $^2T_{2g}(G)$ and $^2T_{1g}(P)$ transitions, but also shows the distinct vibrational progression in the latter peak. The $[Co(NH_3)_6]^{2+}$ spectrum does not show the $^2T_{1g}(G)$ and $^2T_{2g}(G)$ peaks, but is quite similar to the other two complexes in its other bands. It is possible that the two doublet transitions are enhanced in the $[Co(en)_3]^{2+}$ and $[Co(sep)]^{2+}$ absorption spectra due to the deviation from octahedral symmetry in these complexes. It is notable that the doublet states are observed at 16700 and 17600 cm^{-1} in the circular dichroism spectrum [22] of hexaaquacobalt(II).

From the standpoint of this paper, the most important value is the energy of the ^2E state. The transition to this state being interconfigurational and spin-forbidden, this band should be broad and very weak, and occurring in the NIR or IR, it should be extremely difficult to observe. It is not suprising that it is not seen. All calculations involving the energy of this state therefore must rely on estimated values.

Ligand-field Analysis

A conventional ligand-field treatment for octahedral d^7 complexes rationalizes the observed spectra well. Using published values [23] of $B = 835$ cm^{-1}, $C = 4 B$ and $\xi = -450$ cm^{-1}, the spectra of $[Co(NH_3)_6]^{2+}$, $[Co(en)_3]^{2+}$ and $[Co(sep)]^{2+}$ may be fit with the single parameter $10Dq = 9900, 10700$ and 11700 cm^{-1} respectively, with all of the observed transitions fit to within 800 and most to within 200 cm^{-1} (see Table 4). These fits could certainly be improved by adjustment of the Racah parameters and more careful consideration of the trigonal distortion in the latter two complexes, but on the whole the agreement is quite good. In this analysis, the energy of the ^2E state is calculated to be 6800, 6000 and 5000 cm^{-1} for $[Co(NH_3)_6]^{2+}$, $[Co(en)_3]^{2+}$ and $[Co(sep)]^{2+}$, respectively. It should be noted that Stynes and Ibers [16] calculated the ^2E energy

in hexaamminecobalt(II) to be 8600 cm^{-1}, assuming $10Dq = 10100$ cm^{-1}, $B = 900$ cm^{-1} and $C = 4 B$.

The limits on accuracy of these predicted ^2E values are difficult to assess. However, additional evidence supporting the ligand-field derived values for the vertical ^2E energy comes from the study of cobalt(II) complexes with higher ligand fields. The analysis presented here would predict that the spectroscopic ^2E state would cross the ^4T ground state when $10Dq$ is approximately 17500 cm^{-1}. Taking the Jahn–Teller distortion of the ^2E state into account, estimated by Larsson *et al.* [15] to be about 2000 cm^{-1}, spin equilibrium should occur at $10Dq = 15500$ cm^{-1}.

Hexacoordinate low-spin cobalt(II) species are fairly rare. The hexanitro [24], hexakis(isocyanide) [25] and tris(diarsine) [26] complexes are low spin, and spin equilibrium occurs in the bis(terpyridine) complex [24, 27]. The absorption spectrum of the high-spin bis(terpyridine) species [28] shows a weak, broad band around 15000 cm^{-1}. This appears to be the $^4T_{2g}(F)$ transition, and is consistent with a ligand field of about 16000 cm^{-1}. If the ^2E energy were much lower than the value calculated, Co(II) would be expected to be low spin in considerably weaker ligand fields than observed.

Comparison to INDO Results

Larsson *et al.* [15] calculated the energies of the spectroscopic states of $[Co(NH_3)_6]^{2+}$ using a parameterized INDO/S method (an SCF-CI calculation of the INDO/S type), using either the ^2E or ^4T as reference state. A value of 1300–1800 cm^{-1} was added to the calculated ^2E state energy as an empirical correction for a multiplicity effect. Their results are summarized in Table 5, comparing the observed, INDO/S and ligand-field calculated values.

The data suggest that the parameterized INDO/S calculation is not as good as the ligand-field calculation in rationalizing the experimental energies of the Co(II) states. The $^4T_{1g}(P)$ manifold is under-

TABLE 4. Assignment of observed transitions and comparison to ligand-field calculated energies for $[Co(NH_3)_6]^{2+}$, $[Co(en)_3]^{2+}$ and $[Co(sep)]^{2+}$

State	$[Co(NH_3)_6]^{2+}$		$[Co(en)_3]^{2+}$		$[Co(sep)]^{2+}$	
	obs.	calc.	obs.	calc.	obs.	calc.
^2E	a	6800	a	6000	a	5000
$^4T_{2g}(F)$	9350	9400	9900	10000	10990	10800
$^2T_{1g}(G)$	a	14800	15300	14800	14800	14700
$^2T_{2g}(G)$	a	15500	16300	15500	15800	15700
$^2T_{1g}(P)$	18800	19000	19100	19100	18300	19200
$^4T_{1g}(P)$	20500	20500	21200[b]	21200	21300[b]	22000
$^4A_{2g}(F)$	a	19000	a	21000	a	23000

[a]Not observed.   [b]Average of two peaks of split state.

TABLE 5. Comparison of energies of states of $[Co(NH_3)_6]^{2+}$ from ligand-field and INDO/S calculations

State	Experimental[a]	Ligand field[a]	INDO/S[b]
^2E	d	6800	3300–4700[e]
$^4T_{2g}(F)$	9350	9350	8800–9300
$^2T_{1g}(G)$	~15500[c]	14800	11000
$^2T_{2g}(G)$	~16500[c]	15500	f
$^2T_{1g}(P)$	18800	19000	f
$^4T_{1g}(P)$	20500	20500	17500–18100
$^4A_{2g}(F)$	d	19000	19700–21000

[a]From Table 4. [b]Ref. 15. [c]Estimated by comparison to $[Co(en)_3]^{2+}$, $[Co(sep)]^{2+}$ and $[Co(H_2O)_6]^{2+}$. [d]Not observed. [e]After 1300–1800 cm^{-1} correction, see ref. 15. [f]Not given.

estimated by about 2500 cm^{-1} and the $^2T_{1g}(G)$ is underestimated by about 4500 cm^{-1}. The latter value is uncorrected for its multiplicity, but even after correction by 1800 cm^{-1} would still be low by about 2700 cm^{-1}. These values appear to have been accepted originally based on an incorrect assignment [15] of the $[Co(NH_3)_6]^{2+}$ spectrum: the 18 500 cm^{-1} band was assigned to $^4T_1$ and the 20 700 cm^{-1} band to $^4A_2$. The INDO calculated energy (before correction) for the important ^2E state lies 4000 cm^{-1} below the ligand-field value. This discrepancy is similar to the difference between the INDO calculated value for the $^2T_{1g}(G)$ state and the observed value for the transition, suggesting a general trend for doublet states. Considering the overall consistency of the ligand-field treatment, the high ligand-field strength necessary for spin equilibrium in Co(II), and the inaccuracies in the INDO/S prediction, we will adopt the ligand-field calculated energies here.

Electron Self-exchange

In light of the value presented here for the vertical energy of the ^2E state in $[Co(NH_3)_6]^{2+}$ (6800 cm^{-1}) being higher than the value presented by Larsson *et al.* (3300–4800 cm^{-1}), a reconsideration of the participation of the ^2E state in the electron transfer reaction seems in order. As Larsson *et al.* note, the main consideration is whether the ^4T state can cross to the ^2E state as it is compressed towards the transition state. Classical calculations (Marcus–Hush) [29] using the known bond length values of r_{ox}^0 and $r_{red}^0 = 1.96$ [30–33] and 2.18 Å [11] and force constants f_{ox} and $f_{red} = 2.45$ [34] and 1.27 [35] mdyn/Å put the Co–N distance at $r^\dagger = 2.035$ Å in the transition state for the $^4T/^1A$ reaction. The inner-sphere reorganizational energy is calculated to be 73 kJ/mol.

Two terms will be ignored in the activation energy comparisons to be made here. The first is the

quantum reactant–product interaction energy, $\mathcal{H}_{if}$. While its value may vary considerably for the different cases discussed here, it is probably not a large contribution to the activation energy. Newton [4, 5] calculates the one-electron matrix element for $[Co(NH_3)_6]^{3+/2+}$, roughly the value of $\mathcal{H}_{if}$ for the $^2E/^1A$ pathway, to be 940 cm^{-1} with a 7.1 Å center-to-center separation and an ideal alignment. This could contribute to lowering the activation energy by 5 kJ/mol, but the reaction could be adiabatic with a considerably smaller interaction and this full value might not come to bear. Secondly, the effect of tunneling on the rate constant will also be ignored. Sutin and coworkers [12] estimate that tunneling contributes a factor of six to the rate constant of exchange in $[Co(en)_3]^{3+/2+}$, with $\Delta r^0 = 0.21$ Å, and a factor of three to $[Fe(H_2O)_6]^{3+/2+}$ with $\Delta r^0 = 0.13$ Å, amounting only to a relative factor of two over the range of Δr^0 values under consideration here.

Before looking at these calculations, a further point must be noted. In treating the $^1A/^2E$ reaction, the Jahn–Teller distortion of the ^2E state would appear to be a complication. In fact, it is easily dealt with. The decrease in energy from the octahedral ^2E state to the Jahn–Teller distorted state with the same average bond length is estimated by Larsson *et al.* [15] to be approximately 2000 cm^{-1}, based on the octahedral state with $r^0 = 2.20$ Å and the distorted state with axial and equatorial bond lengths of 2.32 and 2.14 Å respectively. The distorted ^2E complex must become more octahedral in conformation in its approach to the transition state. The transition state is thus composed of two slightly tetragonally distorted cobalt molecules. Comparing the octahedral to the distorted activated complex, some of the energy drop for the distorted Co(II) is offset by the energy gain from distortion of the Co(III). In fact, this situation is analogous to lowering the energy of the reactants by 2000 cm^{-1} relative to the products. A Marcus theory view would suggest that the energy of the activated complex for the distorted case will drop relative to that for the octahedral case by about one-quarter of the 2000 cm^{-1} value, or about 6 kJ/mol. Thus, calculations can be performed for the octahedral ^2E state, then simply corrected by this value.

In order to properly evaluate the energetics of the $^2E/^1A$ pathway, in addition to the vertical ^2E energy, the energy of this state as a function of the Co–N distance, r, is needed. This can be approached in two ways. In one approach, the energy can be calculated by ligand-field theory if the relationship between $10Dq$ and r is known. Alternatively, if the minimum-energy Co–N distance and the force constant for the ^2E state are known, its energy is easily calculated at any Co–N distance using a classical model.

Ligand-field Approach

Taking the first approach to the calculation, it can be noted that assuming that the octahedral ^2E and ^4T states have the same value for their symmetrical stretch force constant, the vertical energy difference between the two states is a linear function of the Co–N bond distance, r. Also, according to ligand-field theory, the energy separation decreases linearly as $10Dq$ increases. Thus a roughly linear relationship obtains between $10Dq$ and r. Busch *et al.* [36] and Hambley [37] have commented on the effect of the ligand core size on the spectrum of Co(III).

As Larsson *et al.* point out, $10Dq$ is approximately 10 000 cm^{-1} for the Co(II) state with $r^0 = 2.18$ Å and 21 000 cm^{-1} for the Co(III) state with $r^0 = 1.96$ Å, a change of about 50 000 cm^{-1}/Å. However, it is probably not a good assumption that the ligand-field splitting for cobalt(II) and cobalt(III) at the same Co–N distance will be the same, due to the effect of spin-change on $10Dq$. Jørgensen [38] has estimated that $10Dq$ decreases by as much as 30% when an electron is promoted from a t_{2g} to an e_g orbital. This would lead to a substantial lowering of the $10Dq$ estimate for $r = 1.96$ Å, and a large reduction of the slope of $-10Dq$ versus r. This can be seen by comparing the situation for two different metals in the same ligand field. A good example is to compare hexaaquacobalt and hexaaquairon. For Co(III) and Co(II), $10Dq = 20\,800$ and 8900 cm^{-1} [39, 40]. For Fe(III), $10Dq = 13\,700$ cm^{-1} and $r^0 = 1.99$ Å, and for Fe(II), $10Dq = 10\,400$ cm^{-1} and $r^0 = 2.12$ Å [12, 39].

Comparing ferrous and ferric, the slope $-\Delta(10Dq)/\Delta r^0$ is 25 000 cm^{-1}, only about half the cobaltous/cobaltic value. The iron couple is a high-spin d^6/high-spin d^5 situation as opposed to high-spin d^7/low-spin d^6 for the cobalt couple, and hence avoids the complications from spin change. Another comparison might be the hs d^7 Co(II) with the hs d^6 Fe(II), both with +2 charge. Here the slope is again about 25 000 cm^{-1}/Å.

The octahedral ^2E state is expected to cross the ^4T state at $10Dq = 17\,500$, or about 7700 cm^{-1} above the value for ground state hexaamminecobalt(II). Using a rough estimate value of 30 000 cm^{-1}/Å for the slope of $-10Dq$ versus r in the Co(II) case, the energy difference between the octahedral ^2E and ^4T states at $r^\dagger = 2.035$ Å drops by about 4300 cm^{-1} to about 2500 cm^{-1}; after subtracting 6 kJ/mol for the Jahn–Teller distortion, the ^2E pathway would still be about 23 kJ/mol above the ^4T pathway. Plainly this calculation is entirely dependent on the value of the slope of $10Dq$ versus r, and additional effort should be expended to establish this value. However, it suggests that quite a high value of the slope, about 50 000 cm^{-1}/Å, would be necessary for the two pathways to be equienergetic.

Bond Distance Approach

If a value can be established for r^0 for the octahedral ^2E state of $[Co(NH_3)_6]^{2+}$, the energy of the $^2E/^4T$ pathway can be easily calculated. Larsson *et al.* calculate the equilibrium distances to be 2.14 Å for the ^4T and 2.09 Å for the ^2E. The difference of 0.05 Å is more significant than the absolute values, and leads to an estimate of $r^0(^2E) = 2.13$ Å, which agrees with an estimate by Newton [41]. The symmetrical stretch force constant will be assumed to be 1.27 mdyn/Å, the same value as for the ground state cobalt complex. While it is conceivable that the ^2E value could be somewhat higher, the calculations of Larsson *et al.* do not suggest that it is.

For hexaamminecobalt(II), assuming $r^0(^2E) = 2.13$ Å, the energy minimum for the ^2E state lies 5.7 kJ/mol below the spectroscopic value, thus 75.6 kJ/mol above the ground state. The reorganizational energy of the $^2E/^1A$ path, with $\Delta r^0 = 0.17$ Å, is 43.7 kJ/mol, and subtracting 6 kJ/mol to correct for Jahn–Teller distortion the overall activation energy would be 113 kJ/mol, roughly 40 kJ/mol greater than the $^4T/^1A$ pathway.

The ^2E pathway can be calculated to be equienergetic with the ^4T pathway in the hypothetical case that the value of $r^0(^2E) = 2.08$ Å. This represents a bond length almost halfway between the ground state Co(II) and Co(III) values and lower than the 2.13 Å estimate given above, but one which cannot be ruled out. Thus we again conclude that the ^2E path probably lies above the ^4T, but the two may be close to equienergetic.

Other Reactions

The fact that the ^2E and ^4T pathways may be close in energy makes it difficult to determine the true reaction path. Unfortunately, this near degeneracy is not easily removed by changing ligands. Sepulchratecobalt is a case in point. In this couple, $\Delta r^0 = 0.174$ Å, leading to a calculated $\Delta E_{is}^\dagger$ of 45.7 kJ/mol (assuming the same force constants as for the hexaamminecobalt couple), roughly 27 kJ/mol less than for the hexaamminecobalt couple. This difference accounts for most of the approximately 10^6-fold difference in the observed rate constants of the two couples [42, 43]. The sepulchratecobalt(II) complex does have a stronger ligand field than the hexaammine complex, leading to the estimate presented here for the ^2E vertical energy of 5000 cm^{-1} (59.8 kJ/mol). If the octahedral ^2E state is assumed to have $r^0 = 2.11$ Å, (0.05 Å less than the ground state), and assuming the relevant force constants are the same as for the hexaammine, the overall $\Delta E_{is}^\dagger$ for the $^2E/^1A$ pathway (including Jahn–Teller distortion) is 69.8 kJ/mol, some 24 kJ/mol above the ground state pathway. In order to have the same activation energy as the ground state pathway, $r^0(^2E)$ would have to be approximately 2.075

Å. The low-spin pathway is therefore roughly as accessible in the sepulchrate complex as in the hexaammine couple. The rapid and adiabatic behavior of sepulchrate and related couples thus might also be due to participation of the ^2E state. It is noteworthy, though, that the rapidity of the sepulchrate exchange relative to the hexaammine exchange cannot be due to a more accessible ^2E state, and these reactions are presumably equally adiabatic.

The electron self-exchange rate constants of a variety of cobalt complexes seem consistent with Marcus theory calculations, without the need to invoke a less-than-unity transmission coefficient [7, 8, 12, 14]. There have been several treatments suggesting that the ground state pathway for electron self-exchange in the $[Co(NH_3)_6]^{3+/2+}$ couple must be non-adiabatic [4, 10, 14, 29]. The assumption that this pathway is allowed only through spin—orbit coupling has led to calculated values of the transmission coefficient of 1×10^{-4} by Buhks *et al.* [10] and 4.0×10^{-3} by Newton [4]. We have proposed an alternative hypothesis [44], that the ground state pathway is, in fact, adiabatic and that it is not necessary to involve spin—orbit coupling to allow the reaction. In this view electron transfer may be viewed as a 'three-electron' process without a spin change, although the general assumption has been that such a process would have a very small matrix element and be non-adiabatic [45]. However, this matter has not been thoroughly explored.

It is unfortunate that the coincidental nearness in energy of the ^4T and ^2E paths makes it difficult to determine which is the true pathway of reaction. Knowledge of the transmission coefficient of the ground state reaction would be extremely useful in evaluating the importance of orbital overlap in electron transfer reactions. It is possible that further ligand-field studies or improved calculations using the ligand-field data and assignments presented here may indicate that the energy difference between the two pathways makes them experimentally distinguishable. It might also be possible to study Co(III/II) couples with weaker field ligands than ammines, in which case the ^2E pathway might rise well above the ^4T. In the meantime the question of the adiabaticity of the $^4T/^1A$ pathway of the hexaamminecobalt exchange remains experimentally untested, and this reaction which has created so much confusion for electron transfer theorists is still a partial mystery.

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