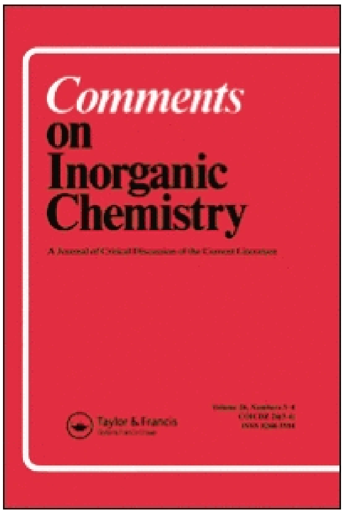

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# On the Role of the High-Spin State in the Water Exchange Reaction of Hexaaquocobalt(III)

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# On the Role of the High-Spin State in the Water Exchange Reaction of Hexaaquocobalt(III)

The potential surface for the $^5T_{2g}$ state of $Co(OH_2)_6^{3+}$, as estimated from spectroscopic data plus some assumptions from the work of Wilson and Solomon on $Co(NH_3)_6^{3+}$, has a minimum that falls about 4 kcal mol$^{-1}$ above the low-spin ground state. The quintet state probably plays a role in the substitutional lability of the aquo ion, as suggested 30 years ago by Taube and coworkers.

Substitution reactions of low-spin octahedral cobalt(III) complexes generally proceed very slowly. Because the activation step in these reactions involves extensive dissociation of the bond to the leaving group, the barrier is quite large for most cobalt(III) complexes, owing to the fact that $^1A_{1g}(t_{2g})^6$ ground states possess very substantial ligand-field stabilization energies.[1] Given this situation, it is somewhat surprising that the low-spin cobalt(III) aquo ion, $Co(OH_2)_6^{3+}$, exchanges coordinated water with water molecules in solution at alarmingly high rates.[2] At 25°C, the rate constant is several orders of magnitude greater than that for water substitution in a 'normal' cobalt(III) complex, $Co(NH_3)_5OH_2^{3+}$. Our comment concerns one simple question: why the difference?

One possible answer to the above question was offered in 1951 by Taube and coworkers, who proposed[2] that the high-spin state of $Co(OH_2)_6^{3+}$, $^5T_{2g}(t_{2g})^4(e_g)^2$, which with two $e_g(\sigma^*)$ electrons should be substitution labile [as, for example, is $Fe(OH_2)_6^{3+}$],[1] may be accessible thermally. Specifically, Taube and coworkers suggested[2] that the labile quintet state might be within 4 kcal mol$^{-1}$ of the ground state.

Fifteen years later, Johnson and Sharpe[3] seemingly ruled out the Taube explanation by performing an electronic spectroscopic analysis of $Co(OH_2)_6^{3+}$ [in $CsCo(SO_4)_2 \cdot 12H_2O$]. The Johnson–Sharpe analysis placed[3] the quintet state at least 14 kcal mol$^{-1}$ above $^1A_{1g}$, but one very critical factor was ignored. *The straight ligand-field analysis yields the vertical excitation energy*, which is a far cry from the difference in energies of the minima of the potential

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curves for the $^1A_{1g}$ and $^5T_{2g}$ states. In assessing Taube's proposal, we are interested in the latter quantity much more than in the vertical transition energy. To address this problem, we have calculated a series of potential curves for the quintet state of $Co(OH_2)_6^{3+}$ using various reasonable assumptions, as outlined below.

The procedure we have adopted follows that of Wilson and Solomon,[4] who employed extensive spectroscopic data to derive potential curves for the $^1T_{1g}$, $^3T_{1g}$, and $^5T_{2g}$ excited states of $Co(NH_3)_6^{3+}$. In this work, the experimentally observed splittings in the electronic origin of the $^3T_{1g}$ state were used to estimate the relative position of the $^5T_{2g}$ potential surface.[4] However, the position of the $^5T_{2g}$ surface also can be estimated from the following expression:

$$\left[\frac{\text{slope}(^5T_{2g})}{\text{slope}(^3T_{1g})}\right]^2 = \frac{Sa_{1g}(^5T_{2g})}{Sa_{1g}(^3T_{1g})}$$

where slope $(^{2S+1}\Gamma)$ is the slope of the $^{2S+1}\Gamma$ state on a Tanabe–Sugano diagram and $Sa_{1g}(^{2S+1}\Gamma)$ is the Huang–Rhys parameter for the $a_{1g}$ normal coordinate in the $^{2S+1}\Gamma$ state. The Tanabe–Sugano slope of the $^5T_{2g}$ state is twice that of the $^3T_{1g}$ state, leading to the following relationship:

$$Sa_{1g}(^5T_{2g}) = 4Sa_{1g}(^3T_{1g}).$$

Wilson and Solomon actually found[4] $Sa_{1g}(^3T_{1g}) = 2.4 \pm 0.8$, yielding $Sa_{1g}(^5T_{2g}) = 9.6 \pm 3.2$. The vertical transition energy is given by

$$E_{FC}(^5T_{2g} \leftarrow {}^1A_{1g}) = 20Dq - 5B - 8C,$$

in which the $Dq$, $b$, and $C$ values are appropriate for the ground-state equilibrium geometry. Finally, the $^5T_{2g}$ force constant for the $a_{1g}$ vibration is assumed to be $k' = \alpha k$ ($k$ = ground-state value), where $0 < \alpha < 1$. Locating the harmonic $^5T_{2g}$ potential surface is then reduced to a problem in analytic geometry. The equations describing the two potential surfaces in Figure 1 are

$$E(^3T_{1g}) = \tfrac{1}{2}kQ^2$$

$$E(^5T_{2g}) = E_0 + \tfrac{1}{2}k'(Q - Q_0)^2$$

The Franck–Condon energy for $^5T_{2g} \leftarrow {}^1A_{1g}$ is just $E(^5T_{2g})$ evaluated at $Q = 0$,

$$E_{FC}(^5T_{2g}) = E_0 + \tfrac{1}{2}k'Q_0^2.$$

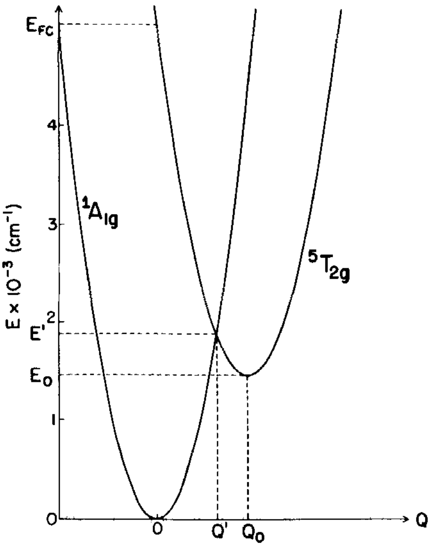

FIGURE 1 Potential energy curves for the $^1A_{1g}$ and $^5T_{2g}$ states of $Co(OH_2)_6^{3+}$.

The Huang–Rhys parameter is defined by

$$S=\frac{1/2k'(\Delta Q)^2}{\hbar\omega'}.$$

Substituting into the expression for $E_{FC}$ in terms of $Dq$, $B$, and $C$ gives the separation of the minima of the $^5T_{2g}$ and $^1A_{1g}$ potential surfaces:

$$E_0=20Dq-5B-8C-\hbar\omega' Sa_{1g}(^5T_{2g}).$$

The uncertainty in $E_0$ depends directly upon the uncertainties in estimating $E_{FC}(^5T_{2g})$, $S(^5T_{2g})$, and $\omega'$. The results, with error limits, of this calculation are set out in Table 1. Our calculated $^5T_{2g}$ potential surface lies in the region of the upper limit of the $^5T_{2g}$ surface derived by Wilson and Solomon.[4] Both $^5T_{2g}$ surfaces, however, produce an $E_0$ for $Co(NH_3)_6^{3+}$ that is greater than 17 kcal $mol^{-1}$.

We are now ready to estimate a $^5T_{2g}$ potential surface for $Co(OH_2)_6^{3+}$, employing the available spectroscopic data along with reasonable assumptions based on the hexaammine analysis. Johnson and Sharpe obtained values of $Dq$, $B$, and $C$ from the reflectance spectrum of $CsCo(SO_4)_2 \cdot 12H_2O$.[3] The value of $Sa_{1g}(^3T_{1g})$ will be assumed to be roughly equal to that in the hexaammine.[4] The $^5T_{2g}$ symmetric vibrational frequency will be taken as 90%

TABLE I
Parameters and calculated $E_{FC}$ and $E_0$ values

| | $Co(NH_3)_6^{3+}$ | $Co(OH_2)_6^{3+}$ |
|---|---|---|
| $E_{FC}$(cm$^{-1}$) | 15 660 ± 500 | 5035 ± 500 |
| $Dq$(cm$^{-1}$) | 2400[a] | 2080[b] |
| $B$(cm$^{-1}$) | 619[a] | 513[b] |
| $C$(cm$^{-1}$) | 3656[a] | 4250[b] |
| $E_0$(cm$^{-1}$) | 11 480 ± 2000<br>(32.8 ± 5.7 kcal mol$^{-1}$) | 1465 ± 1600<br>(4.2 ± 4.6 kcal mol$^{-1}$) |
| $\hbar\omega'$(cm$^{-1}$) | 435[a] | 357[c] |
| $Sa_{1g}$ | 9.6 ± 3.2[a] | 10 ± 3 |

[a] From reference 4.
[b] From reference 3.
[c] Based on $\hbar\omega = 397$ cm$^{-1}$, from V. Ananthanarayanan and A. Danti, J. Mol. Spect. **20**, 88 (1966).

of its ground-state value. Under these assumptions, the $^5T_{2g}$ state is calculated to be at much lower energy in $Co(OH_2)_6^{3+}$ than in $Co(NH_3)_6^{3+}$, our best estimate of $E_0$ being 4.2 kcal mol$^{-1}$ (Table 1). The intersection of the $^1A_{1g}$ and $^5T_{2g}$ potential curves is ca. 5.4 kcal mol$^{-1}$ above the ground state minimum (taking $E_0 = 4.2$ kcal mol$^{-1}$), which is the predicted activation energy for the spin crossover process.

The conclusion that may be reached some 30 years after Taube's paper appeared is that it is indeed likely that the $^5T_{2g}$ state of $Co(OH_2)_6^{3+}$ is thermally accessible. Our results show clearly that the quintet state could easily play the important role Taube suggested for it in the substitutional lability of the aquo ion. The take-home comment is as follows: the spectroscopically measured vertical energy difference between the singlet and quintet surfaces of octahedral cobalt(III) complexes is nowhere near the crossover point of the surfaces and, of course, it is even farther from $E_0$; the kinetic and thermodynamic consequences of these differences can be profound.

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