obtained results that are quantitatively in accord with the mechanism described by eq 4-8 where $K_4 = (1.7 \pm 0.3) \times$

$$\mathrm{PtHClL_2 + SnCl_2 \xrightleftharpoons{K_4} PtH(SnCl_3)L_2} \qquad (4)$$

$$\mathrm{SnCl_2 + Cl^- \xrightleftharpoons{K_5} SnCl_3^-} \qquad (5)$$

$$\mathrm{PtH(SnCl_3)L_2 + SnCl_3^- \xrightleftharpoons{K_6} PtH(SnCl_3)_2L_2^-} \qquad (6)$$

$$\mathrm{PtH(SnCl_3)L_2 + C_2H_4 \xrightarrow{k_7} Pt(C_2H_5)(SnCl_3)L_2} \quad \text{(rate determining)} \qquad (7)$$

$$\mathrm{Pt(C_2H_5)(SnCl_3)L_2 \rightleftarrows Pt(C_2H_5)ClL_2 + SnCl_2} \qquad (8)$$

$10^3\ M^{-1}$, $K_5 = 9 \pm 1\ M^{-1}$, $K_6 = (1.8 \pm 0.3) \times 10^5\ M^{-1}$, and $k_7 = (3.0 \pm 0.5) \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$.[12,13] The failure of excess Cl^- to inhibit the $SnCl_2$ catalysis[13] conclusively rules out the previously admissable alternative interpretation which attributes the catalytic role of $SnCl_2$ (in a manner analogous to that for Ag^+)[3] to the formation of the cationic complex $PtH(C_2H_4)L_2^+$ by promoting displacement of the Cl^- ligand as $SnCl_3^-$.

While Scheme II does derive some support from the above parallel, the alternative interpretation of Scheme I has not been ruled out and the mechanism of the insertion reactions involving the cationic $PtH(C_2H_4)L_2^+$ complex still remains to be conclusively established.

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(12) T. A. Weil, A. Mantovani, and J. Halpern, details to be submitted for publication.

(13) These experiments, performed at 25° and an ionic strength of $5.0 \times 10^{-3}\ M$, maintained with $LiClO_4$, encompassed the concentration ranges 1×10^{-4}–$3 \times 10^{-4}\ M$ $PtHClL_2$, 5×10^{-5}–$2.5 \times 10^{-3}\ M$ $SnCl_2$, 9×10^{-3}–$9 \times 10^{-2}\ M$ C_2H_4, and 1×10^{-4}–$5 \times 10^{-3}\ M$ LiCl.

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Geometrical Distortion and Spin-Orbit Splitting in Excited Transition Metal Complexes[1]

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Sir:

During the last few years the use of transition metal compounds in photochemical and energy-transfer experiments has rapidly expanded. The interpretation of the results often depends upon a knowledge of the relative energies of various excited levels in the systems. Such values are usually estimated from the locations of band maxima of absorption and sometimes of emission spectra. Because huge Stokes shifts are found for d-d transitions in these molecules, as well as uncomfortably large values of the spin-orbit coupling constants ζ, we decided to perform a detailed analysis to determine the energies, geometries, decay parameters, and spin-orbit splittings of the lowest excited levels of a few simple complexes. We report here the results for crystalline $K_3Co(CN)_6$. Experiments on ruthenium(II), osmium(II), iridium(III), and rhodium(III) hexacyanides are also in progress.

Figure 1 shows the 4.2°K emission spectrum of $K_3Co(CN)_6$. The smoothed curve is a computer-generated fit that yields information about the lowest excited level $[E(^3T_1)]$ geometry, the M-CN stretching force constant, and the magnitude of the totally symmetric metal-carbon stretching frequency in both the ground and lowest excited (emitting) level. The fitting procedure was carried out on a function that represented a superposition of all possible vibronic transitions originating from the lowest vibrational state of the lowest excited electronic level $[E(^3T_1)]$. The transitions were assumed to terminate on levels possessing 1 quanta of allowing mode and any number of quanta of the totally symmetric (a_1) M-CN vibrational mode of the $[A_1(^1A_1)]$ electronic ground state. Each vibronic transition was assumed to have a frequency dependence of the form $g(\omega) = \omega^4 e^{-(\omega - \omega_m)^2/a^2}$ where ω_m is the frequency at which the maximum of that vibronic transition intensity occurs and a is an average value for the width of a vibronic transition. The relative intensities of the vibronic transition were assigned using Franck-Condon factors. To calculate these Franck-Condon factors a harmonic oscillator model was used that permitted different frequencies and equilibrium positions to be possessed by the a_1 (M-CN) modes of the ground and excited $[E(^3T_1)]$ levels.

Our spectral fitting technique has yielded the following information. (a) The equilibrium nuclear geometry of the $E(^3T_1)$ excited level is approximately octahedral, but the molecule is expanded. We estimate an increase of about 0.10 Å in the M-C equilibrium distance over the 1.89 Å ground-state value.[2] (b) The a_1 (M-CN) vibrational frequency of the excited $E(^3T_1)$ level is 35% lower than that of the corresponding totally symmetric ground-state vibration. (c) The energy of the nonvertical $A_1 \rightarrow E(^3T_1)$ zero-zero transition lies at or higher than 17.1 kK. Its exact location depends upon whether there is a nontotally symmetric enabling mode for the transition. (d) Our value, calculated from the electronic emission band, for the a_1 (M-CN) ground-state frequency is $420 \pm 5\ \mathrm{cm}^{-1}$. This compares favorably with the latest report of $414\ \mathrm{cm}^{-1}$ obtained from ir spectroscopy.[2,3]

With this information we may calculate the approximate position of the band maximum of the absorption corresponding to the $A_1 \rightarrow E(^3T_1)$ transition; that is, we can calculate the energy of the vertical transition from the ground state to the $E(^3T_1)$ level. This transition is difficult, if not impossible, to observe. The vertical absorption requires approximately $^1/_2 k_u (\Delta Q_{a_1})^2$ more energy than that needed for the zero-zero transition [k_u is the force constant for the upper level and equals $\sqrt{0.65}(2.62\ \mathrm{mdyn/Å})^3$]. The band maximum in absorption is predicted to occur ~3.3 kK higher than the zero-zero transition or at approximately 20.3 kK. The observed *emission* maximum appears at ~14.0 kK. This means that where the vertical transition energy is of importance, an error of 18.3 kcal is introduced by using the emission band maximum to compute its energy. Conversely, for states that are seen only in absorption, an error of half this magnitude may result when it is the zero-zero energy of the relaxed

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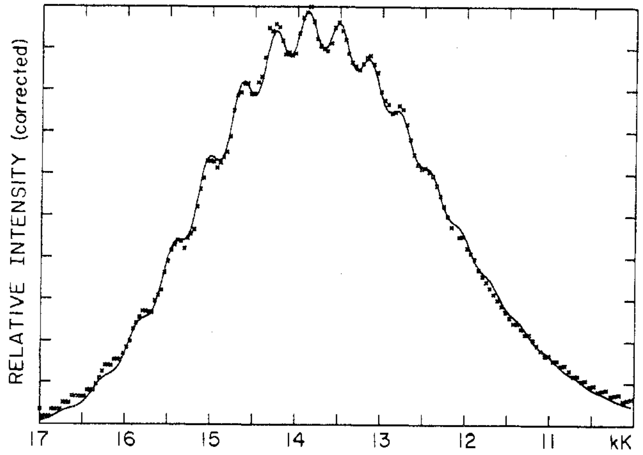

Figure 1. Emission spectrum of solid $K_3Co(CN)_6$ at 4.2°K: X, data points; —, computer fit.

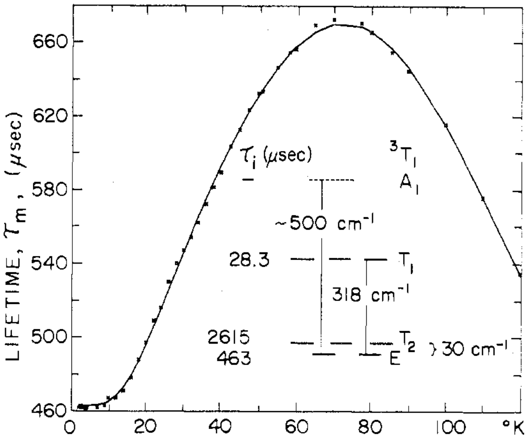

Figure 2. Measured decay times of solid $K_3Co(CN)_6$ as a function of temperature: X, data points; —, computer fit. The decay constants and energy gaps were obtained by a least-squares fit of the equation $\tau_m = [2 + 3e^{-\epsilon_{T_2}/kT} + 3e^{-\epsilon_{T_1}/kT}]/[(2/463) + (3/\tau_{T_2})e^{-\epsilon_{T_2}/kT} + (3/\tau_{T_1})e^{-\epsilon_{T_1}/kT}]$. This method is discussed in ref 7.

excited state that is sought. This change in excited-state geometry and bonding that occurs during relaxation has important significance in the fitting of crystal field parameters. The values of *Dq, A, B,* and *C* will all be different for the excited-state internuclear geometry. In fact, one is virtually dealing with a new molecule.

Admittedly, data of the type obtained here will not be available for many molecules. An approximate method has been proposed,[4,5] however, which although somewhat arbitrary, gives a reasonable estimate for the location of the $K_3Co(CN)_6$ absorption band maximum. The method is simply to add the total width (at ~5% height) of the emission band to the energy of the emission band maximum. In $K_3Co(CN)_6$ the band width is ~6.5 kK, and the emission maximum occurs at ~14 kK, placing the absorption maximum at ~20.5 kK. The agreement with our computed value is very good.

Figure 2 shows the experimental data and computer generated curve of lifetime *vs.* temperature for $K_3Co(CN)_6$. The electronic energy levels and rate constants as obtained from the analysis are included on the figure.[6,7] The position of the uppermost A level was obtained from a computer calculation[8] and was not observed experimentally. The wide range of energies over which the "$^3T_1$" is spread and the large variations in measured rate constants from level to level are intriguing. First, the 30-cm^{-1} E, T_2 split reflects the amount of mixing of other terms of various multiplicities, since these levels are degenerate to first-order in the spin-orbit coupling perturbation. Second, the observed exponentiality of the decay curves down to ~2°K reflects the very rapid Boltzmann equilibration between the levels. Third, the wide span of rate constant values suggests that each of these levels relaxes in a different way and may therefore have unique photochemical behavior.

We have explicitly assumed that our method of data analysis yields energy gaps and decay parameters that pertain to the pure excited electronic levels of the system. For electronically allowed transitions this assumption can be theoretically justified. For a highly symmetrical ion located on a site of low symmetry, the situation is unclear. An *a posteriori* justification for our procedure comes from matching the experimentally obtained levels to those arising from the first-order spin-orbit coupling calculation for the $^3T_1$ term. The procedure yields a value of ~600 cm^{-1} for ζ(3d) of Co^{3+} in this excited configuration, a value that compares favorably with that of the ground state of the Co^{2+} ion.

In summary, one should always use level energies assigned from band maxima in *both* emission and absorption with caution. Depending on the transition energy of interest (vertical absorption, vertical emission, zero-zero, etc.), one could make an error on the order of 10-20 kcal/mol by using uncorrected spectroscopic data. A reasonably accurate method of correcting for this error in a simple way is available, and we urge its adoption.[4,5] Also, the wide ranges of both energies and rate constants of the levels arising from the $^3T_1$ term suggest that the use of the triplet label may be of little value for describing the "state" and that the various levels may have widely different photochemical properties.

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