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Lifetime of the $^4T_{2g}$ State of Chromium(III) Complexes

Sir:

Primary photoprocesses of chromium(III) complex ions in their lowest doublet state, ^2E_g, have been followed through the phosphorescent emission: $^2E_g \rightarrow {}^4A_{2g}$.[1-3] However, except for a few complexes from which fluorescence can be measured, the lowest excited quartet, state $^4T_{2g}$, cannot be similarly studied. Fluorescence is not usually observed if the state ^2E_g lies appreciably lower in energy than $^4T_{2g}$, which is the case for large ligand-field splittings.[4] Delayed fluorescence can also be observed at high temperatures,[3] but fluorescence must always occur; it may go undetected in steady-state experiments because of its continuous broad spectrum and low intensity, as is the case with fluorescence from the lowest singlet excited state of azulene.[5] The important question of what excited state is directly involved in the photoaquation of chromium(III) complex ions[6,7] cannot be answered until more is known about their properties. We present data here on the lifetimes of the ^2E_g and $^4T_{2g}$ states for chromium complexes with various ligands. We also report, from a crude spectrum of the fluorescence of the hexacyanochromate(III) ion, an unexpectedly large Stokes' shift between absorption and emission.

The apparatus used consisted of a condensed flash lamp dissipating about 5 J with a half-width of *ca.* 200 nsec, isolated optically from a monochromator-detector system by complementary filters. At the sensitivities used, no scattered exciting light could be detected. The detector, a Philips 150CVP (S-1 response) photomultiplier, was attached to the exit slit of a Bausch & Lomb monochromator used with a band width of 22 nm. The output of the multiplier was in turn fed into a Tektronix 543B oscilloscope. The time constant of the detector was adjusted, by a capacitor across the load resistor, so as to be less than that of the lifetime studied by a factor of 100. All measurements were made with clear rigid glass solutions at 77°K (either 2:1:1 methanol:water:ethylene glycol or 1:1 methanol:ethanol, depending on solubility). Excitation was into the quartet state manifold of the complexes and the luminescence was generally studied at the known phosphorescence maxima.[8,9]

The luminescence decay curves, when examined at

Figure 1. Oscilloscope traces of luminescence decay: (a) $Cr(acac)_3$, (b) $Cr(CN)_6{}^{3-}$.

slow oscilloscope sweep speeds (*ca.* 0.5 msec/div), show the normal exponential phosphorescence decay. The lifetimes, τ_p, shown in Table I are in good agreement with those of Chatterjee and Forster.[9] At higher sweep speeds (up to 1 μsec/div) there is an *increase* in intensity during the first 50 μsec (see Figure 1a) to a maximum followed by the relatively slow phosphorescence decay. We associate this increase with population of the phosphorescent state *via* intersystem crossing. The lifetime τ_f associated with this initial rise, found by fitting the data to the equation

$$I = A\{e^{-t/\tau_p} + \alpha e^{-t/\tau_f}\} \tag{1}$$

thus represents the lifetime of the lowest excited quartet state, $^4T_{2g}$. The constant α, as will be shown, would have the value -1 if only phosphorescence is observed and a value greater than -1 if both fluorescence and phosphorescence are detected. The data are collected in Table I.

Table I. Reciprocal Lifetimes and Rate Constants (sec^{-1}) in the Luminescence Decay of Chromium(III) Complexes

Complex	$(1/\tau_p)$ $\times 10^{-3}$	$(1/\tau_f)$ $\times 10^{-4}$	k_2 (calcd) $\times 10^{-4}$	α
$[Cr(NCS)_6]^{3-}$	0.23	12	80	-0.47
$[Cr(CN)_6]^{3-}$	0.29	2.0	19	$+1.6^a$
$[Cr(acac)_3]$	2.8	12	36	-0.40
Reineckate ion	3.0	13	72	-0.38
$[Cr(tn)_3]^{3+}$	9.3	13		-0.47
$[Cr(en)_3]^{3+}$	10.0	8.9	70	-0.38

^{a} At 830 nm. Value of α depends on the wavelength monitored.

We assume in the following treatment that the luminescence measured in the decay curves is both fluorescence and phosphorescence. The simple mechanism of DeArmond and Forster[10] gives the following expressions for the intensity of fluorescence and of phosphorescence at any one wavelength as a function

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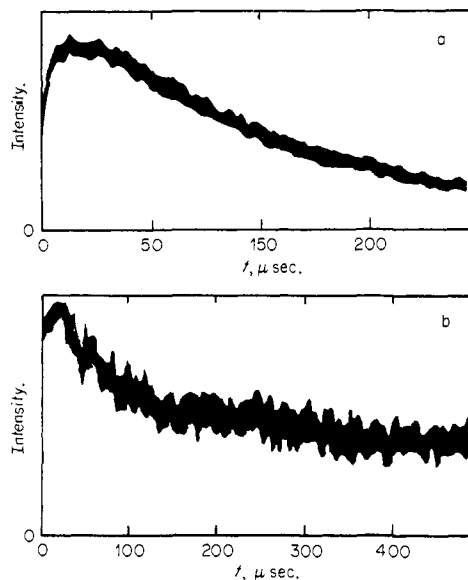(9) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).
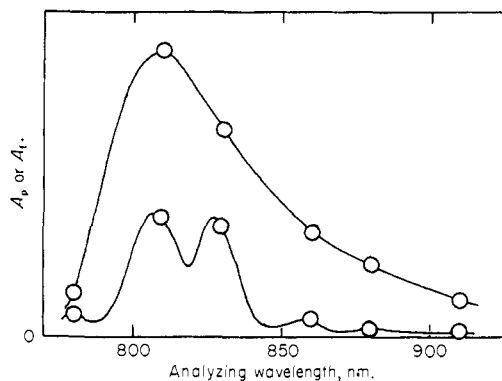(10) L. DeArmond and L. S. Forster, *ibid.*, **19**, 1687 (1963).

Figure 2. Luminescence spectra obtained from decay curves for $[Cr(CN)_6]^{3-}$ in rigid glass solution at 77°K. The upper curve is fluorescence; the lower is phosphorescence with details of the spectrum sketched in from steady-state measurements.

of time after a pulse excitation

$$I_f = A_f \{ e^{-(k_2+k_3+k_4)t} \} \qquad (2)$$

$$I_p = A_p \{ e^{-(k_5+k_6)t} - e^{-(k_2+k_3+k_4)t} \} \qquad (3)$$

The total intensity is

$$I = A_p \{ e^{-(k_5+k_6)t} + [(A_f/A_p) - 1]e^{-(k_2+k_3+k_4)t} \} \qquad (4)$$

which has the same form as eq 1. According to the mechanism, $1/\tau_f$ is the sum of the rate constants for fluorescence, k_2, internal conversion, k_3, and intersystem crossing, k_4. Therefore $1/\tau_f$ sets an upper limit to any one of these rate constants. From data given by Forster,[11] k_2 can be calculated using the oscillator strengths, f, for the transition $^4T_{2g} \leftarrow {}^4A_{2g}$ according to

$$k_2 = n^2 f \bar{\nu}^2 / 1.5 \qquad (5)$$

Calculated values of k_2 are included in Table I. In every case k_2 is larger than $1/\tau_f$, whereas it should in fact be smaller

$$k_2 = \phi_f / \tau_f \qquad (6)$$

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where ϕ_f is the quantum yield of fluorescence. The large discrepancy, even if ϕ_f were 1, which it is not, no doubt reflects the errors inherent in the application of eq 5. Adamson[7] has described in detail the arguments for this disparity based in part on the expected difference in equilibrium configuration of the $^4T_{2g}$ and $^4A_{2g}$ states. For the transition $^2E_g \leftarrow {}^4A_{2g}$, eq 5 does apply because the configurations of the two states are nearly the same.

For only one of the compounds studied here, [Cr(CN)$_6$]$^{3-}$, can we be confident that fluorescence is observed. Not only is α positive, as shown in Figure 1b, but it changes with analyzing wavelength. From the variation of α, the fluorescence spectrum can be derived, as shown in Figure 2, together with the phosphorescence spectrum. The ordinate represents the value of either A_f or A_p. It should be noted that in a steady-state experiment, the intensity of fluorescence would be smaller by a factor of $\tau_p/\tau_f = 70$ than that shown in Figure 2; hence it would almost be impossible to record the fluorescence spectrum by ordinary techniques.

The maximum in the fluorescence spectrum of the cyanide complex at 12,000 cm^{-1} can be compared with the maximum in absorption for the same transition at 26,700 cm^{-1}. This extraordinary Stokes' shift of over 14,000 cm^{-1} implies that the equilibrium configuration of the $^4T_{2g}$ state is indeed very different from that of the ground state. If both states have the same equilibrium symmetry, the metal–ligand separation must be about 0.4 Å larger in $^4T_{2g}$ than in $^4A_{2g}$. The large ligand field splitting of the cyanide ligand arises only partly from a splitting of the electronic states. The rest is caused by the large change in configuration.

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Book Reviews

Peptides 1968. Proceedings of the Ninth European Peptide Symposium, Orsay, France, April 1968. Edited by E. BRICAS, Institut de Biochimie, Faculté des Sciences d'Orsay, Université de Parsi. North-Holland Publishing Co., 305–311 Keizersgracht, Amsterdam, Holland. 1968. xiii + 345 pp. 15.5 × 22.5 cm. $16.00.

This is a collection of some fifty papers presented at the Ninth European Peptide Symposium. Most have bibliographies. The following are the general headings: conformations of peptides and depsipeptides, protecting groups, coupling methods, synthesis of peptides using a polymeric support, synthesis of insulin and analogs, synthesis and structure of other biologically occurring peptides. Most of the papers are in English; a few are in French or German. Participation is by invitation only and regular participants are distinguished European peptide chemists. Each year there are a few guests from the United States and other parts of the world. The group is primarily interested in the synthesis of naturally occurring peptides and their variants. Limited subsidiary interests include such topics as sequence determination, structure problems, and biochemistry.

This and earlier volumes in the series may be characterized as specialized annual reviews of work in selected peptide laboratories. Of particular importance in this volume are reports on recent developments of the Merrifield solid-state technique, an elaboration of the Merck N-carboxyanhydride synthesis, and several papers on refinements of conventional coupling techniques.

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