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A Reexamination of the Wavelength Dependence of Tris(ethylenediamine)chromium(III) Phosphorescence Yields

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Several years ago we reported what appeared to be the first example of an excitation wavelength dependence for the steady-state phosphorescence yield, ϕ_P, of a Cr(III) complex for irradiations within a single absorption band. In particular, we observed significant differences in ϕ_P for 436 and 514 nm excitation into the $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h symmetry) absorption band of $Cr(en)_3^{3+}$ in room temperature aqueous solution ($\phi_P(514)/\phi_P(436) = 0.66$; 25 °C) [1, 2]. It was suggested that 514 nm excitation corresponds to generation of the $^4T_{2g}$ excited state below the cross-over point between the $^4T_{2g}$ and ^2E_g surfaces (Fig. 1). Then, if $^4T_{2g} \rightsquigarrow {}^2E_g$ intersystem crossing (ISC) competes successfully with $^4T_{2g}$ vibrational equilibration, ϕ_{isc} and thus ϕ_P should be larger for excitations above the cross-over point (such as 436 nm). For excitations below this point, ISC would be an activated process due to the small activation barrier imposed by the crossing point (Fig. 1). The suggestion that ISC occurs in competition with $^4T_{2g}$ vibrational equilibration has subsequently received strong support from mode locked laser studies which established Cr(III) ISC as a picosecond process [3–6]. Furthermore, the complexes *trans*-$Cr(en)_2(NCS)_2^+$ and $Cr(bpy)_3^{3+}$ (bpy = 2,2′-bipyridine) have since been shown to exhibit wavelength dependencies similar to $Cr(en)_3^{3+}$ for their steady-state phosphorescence yields [7–9].

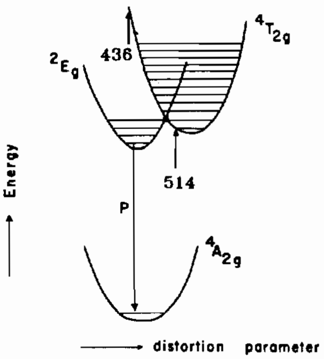

Fig. 1. Hypothetical two-dimensional potential energy diagram for $Cr(en)_3^{3+}$ (P ≡ phosphorescence).

However, Kirk and Namasivayam have very recently reinvestigated the $Cr(en)_3^{3+}$ system employing an argon ion laser for steady-state irradiation; and they report a much smaller wavelength dependence for ϕ_P (≤7%; 21 °C) over the 457.9 to 514.5 nm excitation region [10]. A potentially significant experimental difference between this and our original study was their measurement of steady-state phosphorescence signals under acidic conditions (10^{-2} or 10^{-3} M $HClO_4$) as opposed to our natural pH conditions. Absorbance matched solutions were employed in our study for excitations at 436 and 514 nm; and thus the concentration of $Cr(en)_3^{3+}$ was much higher in the 514 nm case (Fig. 2). The concentration of any free ethylenediamine impurity would therefore also have been higher at 514 nm. Since $Cr(en)_3^{3+}$ phosphorescence is known to be very sensitive to base quenching, the absence of pH control may have led to an erroneously large wavelength dependence for ϕ_P. We have therefore undertaken a reexamination of $Cr(en)_3^{3+}$ steady-state phosphorescence in acidic aqueous solution at 20 °C. In addition to 436 and 514 nm excitation, data have also been obtained on 524 nm irradiation.

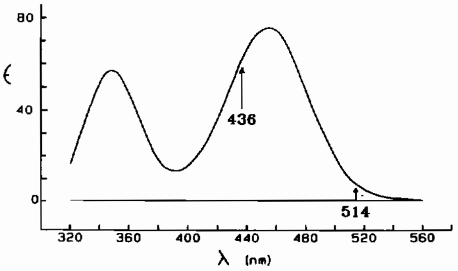

Fig. 2. Ligand field absorption spectrum of $Cr(en)_3^{3+}$ in aqueous solution.

An independent determination of relative phosphorescence yields is also possible via pulse excitation procedures first described by Forster *et al.* [11, 12]. Provided the phosphorescence lifetime, τ, is independent of excitation wavelength, the emission intensity obtained on extrapolation to $t = 0$ after the pulse (I_0) provides a direct measure of variations in ϕ_{isc}. In a recent study, Forster *et al.* utilized this approach in a wavelength dependence investigation of $Cr(en)_3^{3+}$, and obtained results in accord with our earlier steady-state data ($I_0(514)/I_0(470) = 0.55$) [12]. Their investigation was also carried out under natural pH conditions. We therefore felt it important to repeat this pulse excitation study on $Cr(en)_3^{3+}$ in acidic aqueous

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solution at 20 °C. Irradiation wavelengths of 436 and 514 nm (N_2/dye laser) were employed to allow for a direct comparison of phosphorescence data obtained by the steady-state and pulse methods.

Experimental

Materials

The complex $[Cr(en)_3]Cl_3 \cdot 2H_2O$ was prepared according to the literature procedure [13], and samples were recrystallized at least twice. Tris(bipyridine)ruthenium(II)chloride ($[Ru(bpy)_3]Cl_2$) was purchased from G. F. Smith Chemical Company and was used without further purification. The Eastman dyes employed were of laser grade quality.

Relative Phosphorescence Yields

In both the steady-state and pulse excitation studies, percent light absorption by $Cr(en)_3^{3+}$ at the various excitation wavelengths was equalized by absorbance matching at 0.700 ± 0.003. Freshly prepared and filtered solutions of $[Cr(en)_3]Cl_3$ in 0.01 M HCl were prepared for phosphorescence measurements at 20 °C, although no detectable photodecomposition was observed during either study. Relative incident light intensities were determined at the different excitation wavelengths by comparing the emission signals (steady-state or pulsed) of 0.700 absorbance matched aqueous solutions of $Ru(bpy)_3^{2+}$ under identical slit conditions to those used for $Cr(en)_3^{3+}$ measurements [1, 14].

A. Steady State Emission

Relative $Cr(en)_3^{3+}$ steady-state phosphorescence intensity data (530–780 nm) (Fig. 3) were collected using a modified [1] Aminco-Bowman spectrophotofluorimeter (Model 48203D). The instrument employs a 125W Hg–Xe lamp for excitation and a red-sensitive R446S potted photomultiplier tube for detection. Emission spectra were displayed on a Houston 2000 X-Y recorder. The corresponding $Ru(bpy)_3^{2+}$ phosphorescence spectra were recorded immediately prior to and after that of the $Cr(en)_3^{3+}$ system (Fig. 3). For all steady-state studies the slits employed yielded excitation and emission bandwidths of 2.7 and 24 nm, respectively.

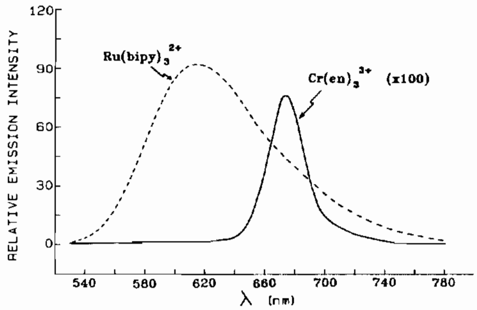

Fig. 3. Relative steady-state emission spectra at 20 °C of absorbance matched (Absorbance = 0.700) solutions of $[Cr(en)_3]Cl_3$ and $[Ru(bpy)_3]Cl_2$ in 0.01 M HCl and water, respectively, on 436 nm excitation.

B. Pulsed Emission

The pulse excitation experiments involved use of a 250 kW N_2 laser (Molectron UV-12) coupled to a Molectron DL-14 dye laser. Excitation wavelengths of 436 nm (in 6th order) and 514 nm (in 5th order) were obtained using 0.01 M ethanol solutions of Coumarin 120 and Coumarin 152 dye, respectively. The pulsed laser light was guided into the sample compartment using a 12 inch quartz fiber light pipe. The $Cr(en)_3^{3+}$ and $Ru(bpy)_3^{2+}$ emissions were monitored at right angles through a J-Y Optics H-10V monochromator (set at 675 nm) followed by a Corning CS 3-66 filter and a RCA 31034A photomultiplier tube. The signals were fed via a load resistor into a Tektronix 5441 storage oscilloscope (with 5A45 amplifier and 5B40 time base plug-ins). A load resistor of value 5kΩ and 1kΩ was used for the phosphorescence decay signals of $Cr(en)_3^{3+}$ and $Ru(bpy)_3^{2+}$, respectively. The emission decays were permanently recorded with a Tektronix C-5C camera loaded with Polaroid 667 film. The desired I_0 values were then obtained by extrapolation of the decay signals to time zero after the excitation pulse.

Results and Discussion

The relative phosphorescence intensities obtained for $Cr(en)_3^{3+}$ at several different excitation wavelengths are given in Tables I and II for steady state

TABLE I. Relative Steady-state Phosphorescence Intensities for 0.01 M HCl Solutions of $[Cr(en)_3]Cl_3$ at 20.0 °C (Absorbance = 0.700, bandpass 2.7 nm).

436 nm Excitation	514 nm Excitation	524 nm Excitation
41.1	33.6	30.0
39.9	33.5	30.2
39.9	33.2	32.4
41.2	32.6	30.6
39.7	35.0	
39.7	34.6	
41.0	34.4	
41.6	33.9	
41.4	35.5	
41.8	32.7	
41.5		
41.1		
Average:		
40.8 ± 0.9[a]	33.9 ± 1.0[a]	3.08 ± 1.1[a]

[a] One standard deviation.

TABLE II. Relative Pulsed Phosphorescence Intensities (I_0) for 0.01 M HCl Solutions of $[Cr(en)_3]Cl_3$ at 20.0 °C (Absorbance = 0.700).

436 nm Excitation	514 nm Excitation	524 nm Excitation
12.5	9.4	9.9
14.1	10.4	9.4
12.2	10.6	10.2
14.1	10.2	9.7
12.4	11.0	
12.6	11.1	
12.7	10.3	
13.1	10.6	
12.9	10.3	
	10.8	
	10.3	
Average:		
13.0 ± 0.7[a]	10.5 ± 0.5[a]	9.8 ± 0.3[a]

[a] One standard deviation.

and pulsed excitation conditions, respectively. A close correspondence is seen between the steady-state and pulse data. For example, values of 0.83 and 0.81 are obtained for the $\phi_P(514)/\phi_P(436)$ and $I_0(514)/I_0(436)$ ratios, respectively. Both these results provide evidence for a significant decrease in ϕ_{isc} at the longer excitation wavelength. The decrease is substantially greater than that obtained in the recent steady-state study of Kirk and Namasivayam [10], and is not readily ascribed to experimental error. However, the wavelength dependence is not as large as that given in our original report ($\phi_P(514)/\phi_P(436)$ = 0.66), and suggests that some base quenching was present in the former study at the longer excitation wavelengths. Our more limited data in Tables I and II for 24 nm excitation are consistent with a further decrease in the value of ϕ_{isc} ($\phi_P(524)/\phi_P(436) = I_0(524)/I_0(436) = 0.75$). Finally, it is noted that the present results for $Cr(en)_3^{3+}$ indicate a comparable wavelength dependence for phosphorescence yield to that previously reported by Gandolfi *et al.* for *trans*-$Cr(en)_2(NCS)_2^+$ ($\phi_P(565)/\phi_P(490)$ = 0.82) [7].

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