Unusual Emission Behaviour of Some Chromium(III) Complexes

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Summary Two phosphorescence bands in room temperature emission in aqueous solutions of $Cr(phen)_3^{3+}$ and $Cr(bipy)_3^{3+}$ are assigned origins from ^2E and ^2T states, the second being a "delayed phosphorescence"; a novel broad band emission from $Cr(bipy)_3^{3+}$ in Me_2SO is assigned as the first example of quartet fluorescence of a Cr^{III} complex in solution.

THE luminescence behaviour of transition-metal complexes has been the subject of numerous investigations in recent years.[1,2] For Cr^{III} complexes such studies have been largely confined to microcrystalline samples and glassy solutions. However, recent work on room temperature fluid phosphorescence[3–8] has been applied with considerable success to the task of distinguishing between quartet and doublet states as precursors to a photochemical reaction.[6–9]

In the course of a photochemical study of the cationic complexes $Cr(phen)_3^{3+}$ and $Cr(bipy)_3^{3+}$ (phen = 1,10-phenanthroline; bipy = 2,2′-bipyridine) we observed that emission originated from several discrete electronic excited states, the composite spectrum being sensitive to temperature and especially solvent. We report here spectra in aqueous and Me_2SO solution recorded either on an Aminco-Bowman SPF equipped with an RCA 446S phototube, or using "Raman" instrumentation based on an argon ion laser.[10]

A significant feature of the room temperature phosphorescence spectra of these two complexes in aqueous solution is the presence of a band to the high-energy side of the principal emission peak. The intense band is assigned as the $^2E \rightarrow {}^4A_2$ 0–0 transition, in agreement with the corresponding absorption spectra (Table). The high energy band is too intense to be attributed to radiative decay from a higher vibrational level of ^2E. We also discount impurity or photoproduct emission, since the relative band areas remain unchanged with sample recrystallization, passage through an anion exchange resin (Cl^-), and irradiation time. Free phen and bipy, and the ultimate complex products *cis*-Cr(phen)$_2$(H$_2$O)$_2^{3+}$ and *cis*-Cr(bipy)$_2$(H$_2$O)$_2^{3+}$ are non-emitters in this region. Moreover, trace amounts of the anions I^-, SCN^-, N_3^-, $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$ (which are efficient, selective doublet quenchers) quench both emission signals. We suggest the high-energy component originates from the higher electronic level $^2T_1$ (*i.e.* $^2T_1 \rightarrow {}^4A_2$ 0–0 transition). This conclusion again draws support from the absorption spectra (Table) The small Stokes shift observed in emission is consonant with the small Jahn–Teller distortion predicted for the $^2T_1$ state. Also, the energy gap ^2E–$^2T_1$ (690 cm^{-1} and 620 cm^{-1} for the bipy and phen cases respectively) is in the range observed in other Cr^{III} complexes.[11,12]

That the $^2T_1$ band becomes more prominent with rising temperature is consistent with upper-level population *via* a Boltzmann type pseudo-equilibrium process and delayed phosphorescence.[13] Examination of the room-temperature solution phosphorescence of Cr(en)$_3^{3+}$ (en = ethylenediamine) also reveals a weak signal at *ca.* 650 nm relative to the strong $^2E \rightarrow {}^4A_2$ 0–0 transition at 672 nm.[14] This high-energy peak is again attributable to emission from the $^2T_1$ state.[15] Although the ^2E–$^2T_1$ energy gap is comparable to that in the Cr(phen)$_3^{3+}$ and Cr(bipy)$_3^{3+}$ systems, the two states now appear not to be in Boltzmann equilibrium. A possible rationalization lies in a much shorter lived ^2E doublet for Cr(en)$_3^{3+}$ (in aqueous solution at 28°C, $\tau = 5 \times 10^{-7}$ s).[16]

We note that emission intensity estimates of the relative $^2T_1$ and ^2E state populations in the phen and bipy cases suggest an upper-state population in substantial excess of Boltzmann predictions. For example, the relative $^2T_1/^2E$ population for Cr(phen)$_3^{3+}$ at 25° C is 21% (from spectra) and 5% (Boltzmann). The discrepancy may result from the assumption of equivalent phosphorescence quantum yields from the two levels. A knowledge of the respective radiative rate constants, k, is important in this regard, and estimates based on absorption band oscillator strengths indicate $k\ (^2T_1) = ca.\ 3{\cdot}3\ k\ (^2E)$. Additional evidence against direct $^2T_1$ emission is the observed absence of the high-energy component at 77 K. Further, similar lifetimes are indicated for the two states, from analysis of data on emission quenching by various added anions.

Addition of Me$_2$SO to aqueous solutions of Cr(phen)$_3^{3+}$ and Cr(bipy)$_3^{3+}$ results in a marked reduction in phosphorescence intensity. Several lines of evidence suggest this results from suppression of $^4T_2 \rightarrow {}^2E$ intersystem crossing (ISC) rather than direct ^2E doublet quenching: (1) Evidence was presented earlier[7] implicating the $^4T_2$ excited state as the reactive level during the photoracemisation of $(+)_{589}$–Cr(phen)$_3^{3+}$. Addition of Me$_2$SO accelerates photoracemisation. (2) The phosphorescence intensity of Cr(bipy)$_3^{3+}$ in water and Me$_2$SO have similar temperature dependencies.[3] A lower activation energy would be anticipated[7] for Me$_2$SO if an essentially temperature-independent doublet-quenching mechanism were operative. (3) In the case of Cr(bipy)$_3^{3+}$, phosphorescence quenching is accompanied by the appearance of a broad structureless emission band centered near 580 nm. We assign this new band to $^4T_2 \rightarrow {}^4A_2$ fluorescence, based on its spectral width and Stokes shift from the $^4A_2 \rightarrow {}^4T_2$ absorption maximum (*ca.* 440 nm). Free-ligand emission was eliminated since the intensity was not irradiation time dependent. (4) CsI addition to a Me$_2$SO–Cr(bipy)$_3^{3+}$ solution quenches the weak phosphorescence signal, but not the broad emission. In view of the doublet quenching capabilities of I^-,[7] Me$_2$SO accelerated back ISC ($^2E \rightarrow {}^4T_2$) is considered unlikely.

TABLE. Absorption and emission maxima of Cr(phen)$_3$Cl$_3$ and Cr(bipy)$_3$Cl$_3$ in water at 25 °C.

	Absorption (10^3 cm^{-1})		Emission (10^3 cm^{-1})		$^2T_1$–^2E
	$^4A_2 \rightarrow {}^2E$	$^4A_2 \rightarrow {}^2T_1$	$^2E \rightarrow {}^4A_2$	$^2T_1 \rightarrow {}^4A_2$	/cm^{-1}
Cr(phen)$_3^{3+}$	13·76	14·47	13·76	14·29	620
Cr(bipy)$_3^{3+}$	13·76	14·51	13·76	14·39	690

If our assignment of $^4T_2 \rightarrow {}^4A_2$ fluorescence in the Cr (bipy)$^3{}_3$+–Me$_2$SO system is correct, this would appear to be the first reported case of room temperature solution fluorescence from a Cr^{III} complex. This has important ramifications regarding solution photochemistry studies. A knowledge of excited-state distortions (as provided by emission data) is vital to any detailed analysis of photochemical behaviour. This is particularly true of the $^4T_2$ excited state, since a compelling body of evidence points to the level being solely responisble for photoreactivity in Cr^{III} systems.[6–9] We note that the fluorescence position is consistent with a correlation between absorption and fluorescence wavelengths for oxygen–ligand–Cr^{III} complexes at low temperature which has been noted.[17]

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