Aquation Quantum Yields of the ^4E and $^4B_2$ Components of the $^4T_{2g}$ state in the Monocyanopenta-aquochromium(III) Ion

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Summary From the variation in aquation quantum yield with excitation wavelength, distinct quantum yields are assigned for the $^4B_2$ and ^4E components of the $^4T_{2g}$ state in $[Cr(CN)(OH_2)_5]^{2+}$; room temperature luminescence excitation spectra rule out doublet state participation in the photoreaction.

ATTEMPTS to identify the excited states responsible for the photochemical reactions of complexes of chromium(III) have produced much evidence indicating that the excited quartet states are the photoactive states.[1–5] Hence the concept of the thermally equilibrated excited (thexi) quartet states has been introduced.[6]

In complexes of O_h symmetry, aquation quantum yields tend to be independent of irradiation wavelength in the region of the first two excited quartet $[^4T_{2g}, {}^4T_{1g}\ (F)]$ bands. Variations of quantum yield with wavelength have been reported for complexes of lower symmetry, implying the involvement of more than one excited state.[7] We report here quantum yield data as a function of wavelength in the region of the first excited quartet state of $[Cr(CN)(OH_2)_5]^{2+}$, together with luminescence excitation spectra and quantum yields.

In a complex of C_{4v} symmetry such as $[Cr(CN)(OH_2)_5]^{2+}$ the $^4T_{2g}$ state splits into $^4E + {}^4B_2$ with the $^4B_2$ state lying lower. The Table gives the measured quantum yields for CN^- release as a function of wavelength from 500 to 650 nm. The band-width of excitation was 1—1·5 nm at each point. The quantum yields have been corrected for any concurrent thermal reaction.[8]

TABLE. Aquation quantum yields for $[Cr(CN)(OH_2)_5]^{2+}$ at 25°C

Wavelength/nm	Quantum yield
500	0·21 ± 0·02
525	0·23 ± 0·02
550	0·25 ± 0·03
575	0·28 ± 0·02
600	0·37 ± 0·03
625	0·44 ± 0·02
650	0·54 ± 0·04

From a Gaussian analysis of the solution absorption spectra[9] and polarized single crystal spectra of $[Cr(CN)(OH_2)_5]SO_4$,[10] we know that 500 nm corresponds to excitation to essentially only the ^4E component of $^4T_{2g}$ while 650 nm corresponds primarily to the $^4B_2$ component. Assuming the ^4E and $^4B_2$ states are not thermally equilibrated we can assign a quantum yield of 0·20 ± 0·04 to the ^4E state and one of 0·55 ± 0·06 to the $^4B_2$ state. An examination of the strong field wave functions shows that the two states are expected to differ in equilibrium geometry and the lack of thermalization is not unexpected.[11]

The $Cr(CN)(OH_2)_5{}^{2+}$ ion shows a weak broadband phosphorescence in aqueous solution at room temperature. The excitation spectrum is very similar to the absorption spectrum, indicative of equal intersystem crossing efficiencies from $^4B_2$ and ^4E to the luminescent state ($^2E + {}^2T_1$ at room temperature).

In addition the luminescence is completely quenched in 0·5 M NaI while the aquation quantum yield decreases by less than 10%. Iodide ion is known selectively to quench doublet states.

The data presented here clearly establish that the photochemical aquation of the $[Cr(CN)(OH_2)_5]^{2+}$ ion arises from the nonequilibrated $^4B_2$ and ^4E states, each of which reacts with its characteristic quantum yield. The lowest doublet states do not appear to be significant in the photoreaction.

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