The $^2E \rightarrow {}^4A_2$ Phosphorescence of Chromium(III) Trisethylenediamine Cation in Aqueous Solution at Room Temperature: Application of Laser Raman Instrumentation

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Summary Aqueous solutions of Cr(en)$_3$Cl$_3$ (en = ethylenediamine) at 25° show emission, when excited by a He–Ne laser as part of a conventional Raman instrument.

IT is well known that low temperature rigid glasses containing the Cr(en)$_3{}^{3+}$ cation show $^2E \rightarrow {}^4A_2$ phosphorescence when suitably stimulated.[1,2] In contrast, although several workers have argued that photochemical reaction of chromium(III) complexes in aqueous solution at ambient temperature involves the ^2E state,[3,4] no phosphorescence has been reported. It has been suggested that the rate of quenching of this state in solution would be very high and sufficient to preclude observation of the phosphorescence.[5]

We now report such emission using a He–Ne laser (632·8 nm, 15,803 cm^{-1}) for excitation. Absorption occurs in the tail of the first spin-allowed band[2,6] in a region where ϵ is *ca.* 0·1. Both sampling and detection employ conventional Spex 1401 Raman instrumentation.

Studies on the rigid glass at 77 K[2] found emission at *ca.* 14,900 cm^{-1} (having appreciable vibronic structure to the red). In aqueous solution of the chloride at 25° we find emission centred on 14,915 ± 5 cm^{-1} (*i.e.* 890 cm^{-1} on the instrument scale) and readily detectable at 0·01 M. Considerable vibronic structure is present with frequencies similar to those found in the rigid glass. A resolution of 10 cm^{-1} was used which is appreciably better than the width of the observed vibronic bands, while the strong 0–0 band could be studied at 2 cm^{-1}. It had a halfwidth of *ca.* 80 cm^{-1}.

All spectra were run rapidly after being made up to minimise the effects of aquation. Much greater stability under irradiation was found for acidified solutions.

Similar 0–0 band positions and halfwidths to those in water were found for solutions of the iodide in dimethyl sulphoxide, dimethylformamide, or dimethylacetamide.

A study of a range of salts of the Cr(en)$_3{}^{3+}$ cation in the solid state demonstrates the presence of emission in this phase too using laser excitation and conventional Raman apparatus. When cooled the 0–0 transition shows fine structure under high resolution (0·5—2 cm^{-1}). Although unresolved at room temperature or above the presence of more than one component is indicated by polarised single crystal work. This fine structure could, for example, be associated with either splitting of the ^2E level[7] or in some cases to exciton coupling in the solid state.

The high intensity of emission in the solids distinguishes it from any Raman spectral bands of the compounds studied (it is rather difficult to obtain any Raman spectra from the highly phosphorescing species). However, in solution where the Raman spectra from some of the dipolar aprotic solvents compares in intensity with the emission we have found study of the depolarisation ratio a usefu method of distinguishing the two phenomena. For polarised incident light Raman modes give ρ between 0 and 6/7, whilst the emission gives a depolarisation ratio that closely approximates to unity.

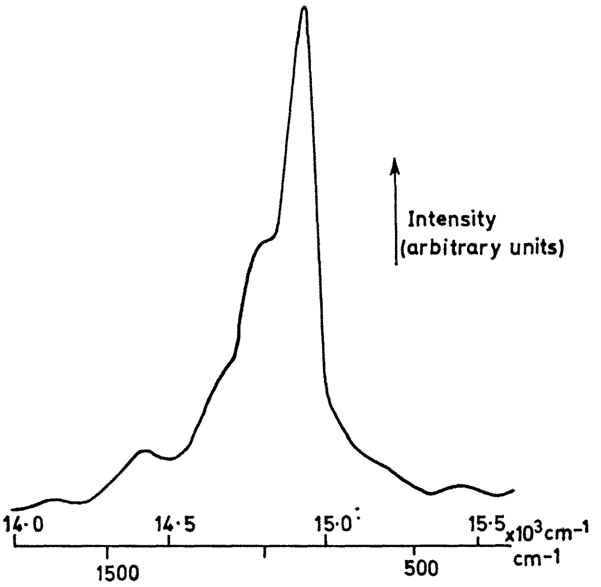

FIGURE. *Emission from* 0·5 M-Cr(en)$_3$Cl$_3$ *in water at* 25°. *The upper scale gives the absolute wavenumber; the lower scale is the normal Raman scale based on* 15,803 cm^{-1}.

Cr(en)$_3$Cl$_3$ was prepared by the method of Gillard and Mitchell[8] and twice recrystallised. It had a satisfactory elemental analysis.

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