

The Circularly Polarised Luminescence Spectrum of $[\text{Cr}(\text{en})_3]^{3+}$ in the Uniaxial Single Crystal Host $2[\text{Rh}(\text{en})_3\text{Cl}_3]\cdot\text{NaCl}\cdot 6\text{H}_2\text{O}$

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The circularly polarised luminescence spectrum of a transition metal ion complex in a uniaxial single crystal host has been measured for the first time; individual vibronic lines of the $[\text{Cr}(\text{en})_3]^{3+}$ (en = ethylenediamine) emission spectrum were found to be circularly polarised and two distinct chiral emitting species were detected.

Circularly polarised luminescence spectroscopy (c.p.l.) is a relatively new technique.¹ By measuring the circular polarisation of the luminescence from an optically active compound information may be obtained about the chirality of the emitting state, which is complementary to that obtained for the ground state by circular dichroism (c.d.) spectroscopy. Despite the advantage of luminescence over absorption spectra in frequently showing more highly resolved vibronic structure, all but one reports of c.p.l. spectra have been for compounds in solution, the single exception being a partial spectrum² of the uranyl ion in the cubic crystal $\text{NaUO}_2\cdot(\text{MeCO}_2)_3$.

The precise mechanism (or mechanisms) whereby tris-chelated transition metal ions gain rotational strength is still

a matter of dispute. The rôle of vibronic coupling, first suggested by Denning,³ has still not been adequately clarified.⁴ The major progress which has been made, however, is largely based on single crystal c.d. measurements^{3,5,6} and we feel that the complementary c.p.l. spectra of transition metal ion complexes in single crystal hosts will add substantially to that progress.

We report the first c.p.l. spectrum of a tris-chelate transition metal ion complex in a uniaxial single crystal host: $[\text{Cr}(\text{en})_3]^{3+}$ (en = ethylenediamine) in $2[\text{Rh}(\text{en})_3\text{Cl}_3]\cdot\text{NaCl}\cdot 6\text{H}_2\text{O}$. Figure 1 shows the unpolarised luminescence and c.p.l. spectra of the $\Delta(-)$ isomer at 200 K. The strongest feature in the spectrum is the partially resolved electronic origin emission at about $14\,900\text{ cm}^{-1}$, ${}^4\text{A}_2 \leftarrow \bar{\text{E}}(^2\text{E})$ and $2\text{A}(^2\text{E})$

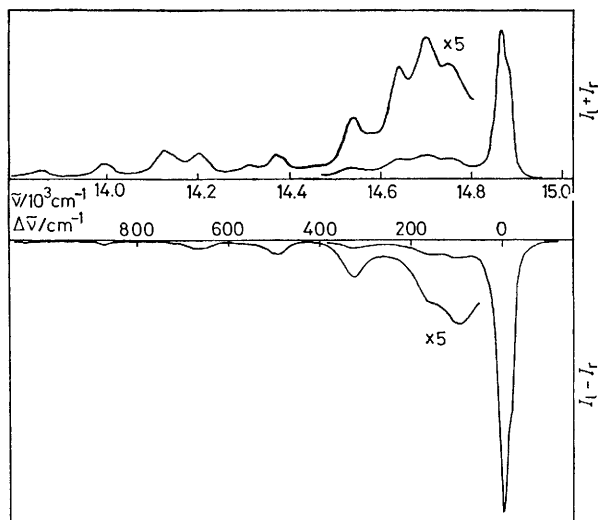


Figure 1. The unpolarised emission (upper curve) and c.p.l. (lower curve) spectra of about 10% $\Delta(-)$ -[Cr(en)₃Cl₃] doped into a single crystal of 2[Rh(en)₃Cl₃].NaCl.6H₂O at 200 K. The sample was excited with *ca.* 30 mW of 488.0 nm radiation from an argon ion laser. Absolute values of g_{em} were obtained by calibrating each spectrum against the circular depolarisation ratio of the ν_1 (A_1) Raman band of CCl₄.

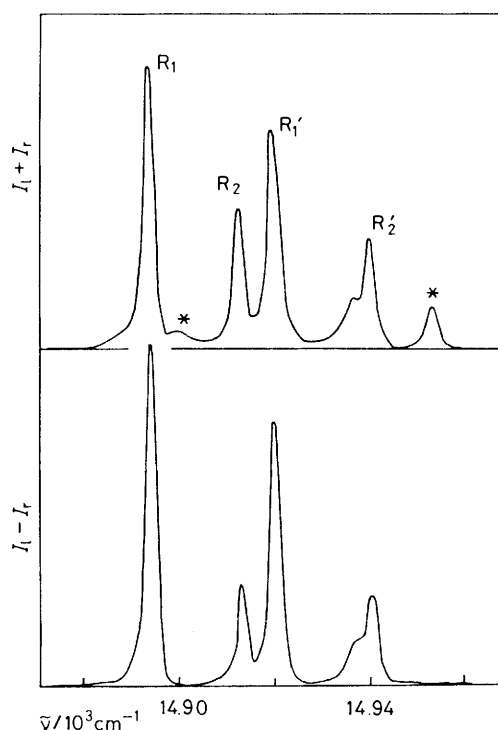


Figure 2. The unpolarised emission (upper curve) and c.p.l. (lower curve) spectra of about 10% $\Lambda(+)$ -[Cr(en)₃Cl₃] doped into a single crystal of 2[Rh(en)₃Cl₃].NaCl.6H₂O at 40 K. The lines marked with an asterisk are not present when the spectrum of a pre-cooled sample is initially run but gradually grow in intensity with irradiation.

(commonly called the R_1 and R_2 lines respectively). The luminescence dissymmetry factor g_{em} ($2\Delta I/I$) at the maximum of the unresolved band (essentially that of the R_1 line) has a value of -0.19 which is very similar to that recently reported for the c.d. dissymmetry factor g_{abs} ($\Delta\epsilon/\epsilon$) of [Cr(en)₃]³⁺ in the analogous iridium host ($g_{abs} = 0.22$).⁷ At 200 K the vibronic structure is sufficiently well resolved to

enable the c.p.l. of individual vibronic lines to be measured. The g_{em} values vary from *ca.* 0 to -0.11 but are never as large as those of the electronic origins. The vibronic structure of the [Cr(en)₃Cl₃] luminescence spectrum has not yet been assigned with certainty. There is general agreement that the 495 cm^{-1} interval is that of the totally symmetric Cr–N stretching mode (of A_1 symmetry) and the vibronic line based on this interval has the largest g_{em} value in the spectrum. The corresponding vibronic line in the c.d. spectrum of [Cr(en)₃]³⁺ in the iridium host has a g_{abs} value of 0.81, nearly four times greater than that of the origin line upon which it is built. Since our c.p.l. spectrum shows no vibronic lines having g_{em} values larger than those of their respective origins, the comment by Flint and Mathews⁸ that the 495 cm^{-1} vibronic line is heavily mixed with the 2T_1 electronic origin in the absorption spectrum receives experimental support.

Flint and Mathews found the emission spectrum of 2[Cr(en)₃Cl₃].KCl.6H₂O to be complicated by emission from photoproducts and from Cr^{III} impurity sites both of which acts as traps at low temperatures.⁸ We find, in agreement with this, that on cooling to 40 K a considerable emission appears at *ca.* 14 700–14 400 cm^{-1} which is not circularly polarised. We find also that at that temperature two sets of origin lines appear [Figure 2, the spectrum is of the $\Lambda(+)$ isomer]. The lines which remain and grow in intensity on raising the temperature (R_1 and R_2) are of the major $\Lambda(+)$ -[Cr(en)₃Cl₃] species; the other pair, labelled R_1' and R_2' , have the same g_{em} values as R_1 and R_2 and so must originate from a minority species of $\Lambda(+)$ -[Cr(en)₃Cl₃] with slightly higher energy. The conformation of the major [Cr(en)₃]³⁺ species in the host crystal is likely to be *tris-lel* [$\Lambda(\delta\delta\delta)$] and it is possible that the minority species is another conformational isomer of the complex. The relatively large energy difference (26 cm^{-1}) between the electronic origins of the intraconfigurational transition seems excessive for a conformational energy difference and a more probable explanation is that the emission is from a molecule of $\Lambda(-\delta\delta\delta)$ -[Cr(en)₃]³⁺ at a different site in the host crystal, possibly a pair or cluster of the guest ions. The two lines marked with asterisks in Figure 2 grow in intensity on prolonged irradiation and are not circularly polarised. They are clearly due to emission from photolysis products which are either achiral or are oriented such that their emission is depolarised.

It is interesting to note that the ratio of g_{em} for the R_1 and R_2 lines (1.64) is very close to the theoretical value of 5/3 (1.67) whereas in the c.d. spectrum in the iridium host the ratio was found to be only 1.1.

We have demonstrated that c.p.l. spectroscopy is a powerful technique for studying both the vibronic optical activity of transition metal complexes and for investigating the distribution of chiral emitting sites in a single crystal host.

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