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Site-Selective Luminescence and Excitation Spectroscopy in $[Cr(NH_3)_5Cl]Cl_2$. Clear Confirmation of a Large ^2E Splitting

Sir:

The large splitting of the $(t_2{}^3)$ state ^2E ($\sim$100–300 cm^{-1}) observed in tetragonal chromium(III) complexes[1-3] has been called into question in ref 4. A 16-cm^{-1} splitting of the lowest energy transition in $[Cr(NH_3)_5Cl]Cl_2$ has been reported, and the lines have been assigned to the two components of ^2E. This is in contrast to the 175 ± 7 cm^{-1} splitting reported in ref 1. A small splitting of the lowest energy transition in $[Cr(NH_3)_5Cl]Cl_2$ was observed as well by other workers.[5] Two transitions separated by 12 ± 1 cm^{-1} with similar oscillator strengths were found in a highly resolved absorption spectrum.[5] However, in this latter work the suggestion has been put forward that these two transitions are due to the R_1 lines of two nonequivalent sites. This was based on some spectroscopic and X-ray results.

The present work reports the results of site-selective spectroscopy in $[Cr(NH_3)_5Cl]Cl_2$ and a comparison with the luminescence and excitation spectra of $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$, which is isostructural at room temperature.[6] The suggestion[5] of two nonequivalent sites in $[Cr(NH_3)_5Cl]Cl_2$ is established by site-selective spectroscopy, and the large splitting of ^2E found in ref 1 is confirmed. A basic treatment of site-selective spectroscopy has been given in ref 7.

$[Cr(NH_3)_5Cl]Cl_2$ and $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$ (1%) were prepared and crystallized as described elsewhere.[5,8,9]

The main components of the experimental equipment were a N_2 laser (PRA LN 1000) pumped dye laser (PRA LN 107), a double monochromator (Spex 1404), a boxcar integrator (SRS SR250), a digital oscilloscope (Tektronix 2430), and a gated[10] photomultiplier tube (EMI 9558).

Figure 1 shows the highly resolved luminescence and excitation spectra of $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$ (1%) in the region of the R_1 line at 12 K. No splitting is observed, and the luminescence and excitation lines exactly coincide (fwhm ≈ 6 cm^{-1}). The shape and the position of the luminescence line do *not* change in the experimental temperature interval 8–35 K, providing further evidence that there is no nearby lying higher excited state. The insert shows an excitation spectrum in the region of R_2. The splitting of ^2E is found to be 178 ± 1 cm^{-1}.

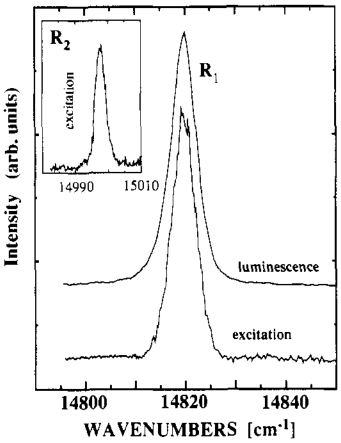

Figure 1. Luminescence (excited at 19 600 cm^{-1}) and excitation spectra (monitored at 14 515 ± 2 cm^{-1}) of $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$ at 12 K in the region of the lowest energy transition. The insert shows the excitation spectrum (R_1 line monitored) in the region of the R_2 line.

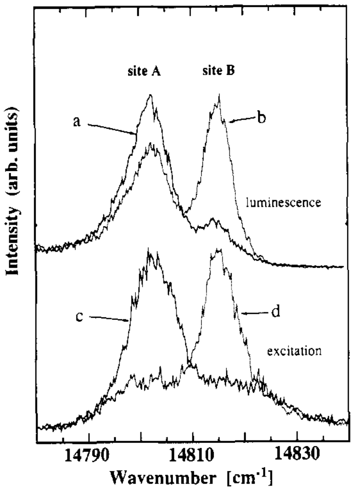

Figure 2. Selectively excited luminescence spectra (excited at (a) 14 986 cm^{-1} and (b) 14 992 cm^{-1}) and selective excitation spectra (vibrational sidebands monitored at (c) 14 493 cm^{-1} and (d) 14 508 cm^{-1}) of $[Cr(NH_3)_5Cl]Cl_2$ at 10 K in the region of the lowest energy transition(s).

Although the R_1 line in $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$ is quite narrow, there still remains an inhomogeneous broadening. Luminescence and excitation lines could be narrowed considerably[11] by using appropriate techniques.[12]

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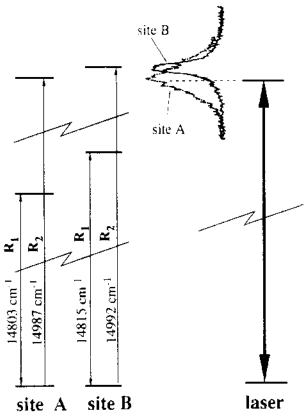

Figure 3. Schematic representation of the experimental results found for $[Cr(NH_3)_5Cl]Cl_2$ at 10 K. Selective excitation spectra of R_2 for site A and site B are shown (R_1 luminescence of site A and site B monitored respectively). The chromophore A is preferentially excited when the indicated laser wavelength is chosen.

From the spectra shown in Figure 1 it is obvious that the observed[4,5] splitting of the lowest energy transition in $[Cr(NH_3)_5Cl]Cl_2$ must be due to different sites. This is clearly illustrated in Figure 2, where the selectively excited luminescence spectra are shown together with selective excitation spectra in the region of the lowest energy transition at 10 K. From these spectra we can conclude that the two transitions at 14 803 and 14 815 cm^{-1} *cannot* belong to the same chromophoric unit and the assignment to R_1 and R_2 as made in ref 4 is thus incorrect. Figure 3 gives a schematic representation of our results found for $[Cr(NH_3)_5Cl]Cl_2$ at 10 K. Spectrum a in Figure 2 was obtained by setting the laser on a wavelength that mainly excites in R_2 of site A. After a nonradiative relaxation process to the lowest excited level luminescence occurs preferentially out of site A. Since R_2 of site A is much broader than R_2 of site B and there is a considerable overlap of the two lines, it is not possible to obtain *non*resonantly a pure site B luminescence spectrum. Excitation energy transfer *between* the two sites is not important at 10 K. This is revealed by the selectivity with which the individual excitation spectra of the two sites can be obtained.[13-15]

However, excitation energy transfer to "killer" traps is the dominating process for the deactivation of the lowest excited state in $[Cr(NH_3)_5Cl]Cl_2$.[11] This follows from an analysis of luminescence decay curves, which show non-single-exponential behavior in $[Cr(NH_3)_5Cl]Cl_2$ and a much shorter lifetime than in $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$.

The observed splitting $\Delta E(R_2 - R_1)$ in $[Cr(NH_3)_5Cl]Cl_2$ is 184 ± 1 and 177 ± 1 cm^{-1} for site A and site B, respectively. The splitting and the absolute energies of the R lines of site B suggest this site to be closely related to the one in $[Rh(NH_3)_5Cl]Cl_2/Cr^{III}$.

The above results encouraged us to investigate the ^2E splitting in $[Cr(NH_3)_5H_2O](ClO_4)_3$. In ref 16 a small splitting of 20 ± 10 cm^{-1} was given. The error indicates that the spectrum could not be resolved. However, using line narrowing techniques, we were able to show[11] that the actual splitting is 206 ± 5 cm^{-1}, in perfect agreement with ref 1.

Large $^2E(t_2{}^3)$ splittings of tetragonal chromium(III) complexes are thus unequivocally established. A more complete treatment of electronic repulsion including nonspherical Racah *B* parameters can rationalize the experimental finding as first suggested in ref 1 and worked out in more detail in ref 5.

A more detailed account of the present work including nonresonant and resonant line-narrowing experiments will be given elsewhere.[11]

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