# Observation of Non-Radiative Energy Transfer from $Cr(NH_3)_6^{3+}$ to $Cr(NH_3)_5Cl^{2+}$

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*Summary* The long (60 $\mu$s) risetime of the $^2E \rightarrow {}^4A_2$ phosphorescence of $Cr(NH_3)_5Cl^{2+}$ in $Cr(NH_3)_6(ClO_4)_3$ indicates that the emissive state is populated intermolecularly.

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INTERMOLECULAR energy transfer has frequently been observed in organic crystals[1,2] and in solid rare earth compounds[3] although the mechanisms of the processes are not well understood.[4] The experimental evidence for interionic transfer in crystalline transition metal compounds is less clear. Efficient non-radiative transfer has been observed between both equivalent and non-equivalent $Cr^{3+}$ ions in oxide lattices[5,6] and there is evidence for energy transfer in $2Cr(en)_3{\cdot}KCl{\cdot}6H_2O$ (en = ethylenediamine).[7] However experiments apparently supporting non-radiative transfer in $Cr(antipyrine)_6{\cdot}Cr(CN)_6$ and similar systems[8,9] has been reinterpreted[10] in terms of a change in the lattice surrounding the anion. This work provides the first unambiguous evidence for energy transfer between well defined complex ions.

At 80 K the $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence decay curve of carefully purified $Cr(NH_3)_6(ClO_4)_3$ was exponential and independent of the wavelength of observation with a half-life of $22{\cdot}0 \pm 0{\cdot}5\,\mu s$ ($k^{80} = 3{\cdot}2 \times 10^4\,s^{-1}$) and a time to maximum intensity of less than 3 $\mu$s. Precipitation of $Cr(NH_3)_6(ClO_4)_3$ from an aqueous solution of pure $Cr(NH_3)_6(NO_3)_3$ in which a trace of $[Cr(NH_3)_5Cl]Cl_2$ had been dissolved yielded a homogeneous crystalline solid containing less than 1% of $Cr(NH_3)_5Cl^{2+}$. The 80 K phosphorescence spectrum of this solid showed strong lines at 14,770 $cm^{-1}$, 14,580 $cm^{-1}$ and 14,460 $cm^{-1}$ in addition to the weaker hexa-ammine lines.[11] The positions and relative intensities of these strong lines were similar to the three strongest lines in the 80 K luminescence spectra of $Cr(NH_3)_5Cl^{2+}$ salts indicating that the chloropenta-ammine ion is not strongly perturbed by incorporation in the $Cr(NH_3)_6(ClO_4)_3$ lattice. The 80 K phosphorescence decay curves were dependent on the wavelength of observation. At the chloropenta-ammine emission peaks the time to maximum intensity was *ca.* 60 $\mu$s and the decay curve is accurately described by equation (1). At regions of the luminescence spectrum

$$I(t) = I_0[\exp(-k_1 t) - \exp(-k_2 t)] \qquad (1)$$

$$k_1^{80} = 5{\cdot}0 \times 10^3\,s^{-1} \text{ and } k_2^{80} = 4{\cdot}5 \times 10^4\,s^{-1}.$$

where the hexa-ammine bands predominate the decay curve was similar to that of the pure hexa-ammine but with $k^{80} = 3{\cdot}3 \times 10^4\,s^{-1}$; elsewhere the complex decay curve could be fitted using an equation[12] representing the sum of the two processes. This risetime of the chloropenta-ammine phosphorescence is two orders of magnitude too long for the populating process of the $^2E_g(O_h)$ state to be intraionic (the experimental risetime of pure $[Cr(NH_3)_5Cl]Cl_2$ phosphorescence at 80 K is less than 3 $\mu$s). This and the similarity of the populating rate constant $k_1^{80}$ to the hexa-ammine decay constant indicates that the chloropenta-ammine $^2E_g$ state is populated by non-radiative energy transfer from the hexa-ammine $^2E_g$ state. The low concentration of chloropenta-ammine and small crystal size eliminates the possibility that the transfer is radiative. Exact agreement between these rate constants would only be expected if energy transfer between all hexa-ammine ions was fast compared to hexa-ammine → chloropenta-ammine transfer and only the $^2E_g$ states of the ions are involved. The distortion of the hexa-ammine lattice by the presence of the chloropenta-ammine ions and the consequent charge balance may also be important. These results were independent of the wavelength of the excitation pulse.[12] The slow luminescence rise is unambiguous evidence for interionic excitation. Spectral measurements alone cannot be used in these systems.[8,9,10]

Raising the temperature above 80 K caused a rapid decrease in the intensity of the penta-ammine emission until at room temperature (300 K) only the hexa-ammine emission can be detected with $k^{300} = 5{\cdot}3 \times 10^4\ s^{-1}$. As expected, this is slightly faster than for the pure hexa-ammine ($k^{300} = 4{\cdot}0 \times 10^4\ s^{-1}$). The quenching of the penta-ammine phosphorescence at room temperature parallels the behaviour of pure $[Cr(NH_3)_5Cl]Cl_2$, which shows only very weak emission at 300 K. Thus energy transfer probably still occurs at 300 K but the chloropenta-ammine emission is quenched by rapid internal conversion from the $^4T_{2g}(O_h)$ state.

$Cr(ND_3)_6(ClO_4)_3$ containing a trace of $Cr(ND_3)_5Cl^{2+}$ shows the same phenomena. The risetime of the chlorodeutericpenta-ammine emission is increased to *ca* 400 $\mu$s at 80 K ($k_1^{80} = 8{\cdot}0 \times 10^2\ s^{-1}$, $k_2^{80} = 5{\cdot}2 \times 10^3\ s^{-1}$) and $k^{80}$ for the deuteriohexa-ammine emission in these samples is similar to the value of $k_2^{80}$. The half-life of pure $Cr(ND_3)_6(ClO_4)_3$ at 80 K is 460 $\mu$s ($k^{80} = 1{\cdot}5 \times 10^3\ s^{-1}$). Thus deuteriohexa-ammine → deuteriohexa-ammine and deuteriohexa-ammine → deuteriopenta-ammine transfer both compete more effectively with the deuteriohexa-ammine $^2E_g \rightarrow {}^4A_{2g}$ radiationless transition than the corresponding processes in the non-deuteriated samples. This is as expected if a transfer mechanism of the type suggested by Dexter[13] is operative. Unfortunately the penta-ammine ions in the deuteriated system are photosensitive which makes precise measurements difficult. Energy transfer to several other impurity ions from $Cr(NH_3)_6^{3+}$ has been observed and we are investigating these systems to find an acceptor suitable for detailed study.

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