Luminescence Intensity of Tervalent Chromium Complexes

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Summary The relative intensity of luminescence at room temperature for tervalent chromium complexes is shown to be largely dependent on the thermal relaxation process $^2E \rightsquigarrow {}^4T_2$.

THE importance of thermal repopulation $^2E \rightsquigarrow {}^4T_2$ as one of the relaxation processes of the ^2E (luminescence emitting) state has been discussed for a limited number of tervalent chromium complexes.[1,2] If the ^2E state is depopulated *via* the $^4T_2$ state, and this is the major relaxation process, the variation of luminescence intensities with temperature should provide a measure of this thermally activated process, and this in turn should be related to the magnitude of the $^4T_2$–^2E energy interval.

We report here the nature of the temperature-dependence of luminescence emission for a series of tervalent chromium complexes in the solid state (see Table).

TABLE

Complex	ΔE(kK)[a]	Form of intensity/temperature curve	$\frac{I_{77}}{I_{350}}$
$Cr(urea)_6(ClO_4)_3$	*ca.* 0	Strong temperature-dependence	∞
$NaMgCr(ox)_3,9H_2O$	1—3	„	∞
$Cr(acac)_3$		„	∞
$K_3Cr(NCS)_6,4H_2O$		Moderate temperature-dependence	25
$Cr(en)_3(ClO_4)_3$	4—5	Weak temperature-dependence	3
$Cr(NH_3)_6Cl_3$		„	*ca.* 2[b]
$K_3Cr(CN)_6$	>10	Approx. zero temperature-dependence	*ca.* 1

ox = oxalate, acac = acetylacetonate, en = ethylenediamine.

[a] Estimates for ΔE, the difference in zero-point energies of ^2E and $^4T_2$ were made from absorption spectra assuming a band-width for the $^4A_2 \rightarrow {}^4T_2$ band of *ca.* 4kK and are approximate only.

[b] This value is approximate due to the very rapid photodecomposition of $Cr(NH_3)_6Cl_3$.

For complexes with oxygen-co-ordinated ligands, the temperature-dependence of emission intensity is very marked. No luminescence could be observed at room temperature. In these cases ΔE is small and the thermal depopulation process will dominate.

On the other hand, complexes with nitrogen- or carbon-co-ordinated ligands generally exhibit limited temperature-dependence. Luminescence at room temperature could be observed from these complexes. Here, with increased values of ΔE, the ability of the thermal process to depopulate the ^2E state is decreased.

Further, while the intensities vary very markedly at room temperature, at liquid-helium temperature we have observed that the emission intensities are generally comparable for the range of complexes studied.

Although thermal relaxation to the $^4T_2$ state is by no means the only process depopulating the ^2E state, we suggest that this mechanism provides an explanation for the wide range of room-temperature emission intensities observed for tervalent chromium complexes.

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