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Room-temperature Luminescence of Tervalent Chromium Complexes

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THE luminescence emission at low temperatures from many tervalent chromium complexes dissolved in rigid glasses has been studied extensively.[1–8] Emission at low temperatures from some solids has also been reported.[9,10] Hitherto it has been considered that thermal deactivation processes limit or entirely quench emission at ambient temperatures.

We have observed strong emission from crystalline powders at room temperature for the complexes listed in the Table.

The intensities of emission appear to be comparable for all the complexes studied with the exception of $[Cr(NH_3)_6]^{3+}$, which relatively is a weak emitter. By contrast, no emission could be detected for $[Cr(acac)_3]^0$ and $[Cr\,ox_3]^{3+}$, although these complexes clearly exhibit luminescence at low temperatures.[5] These results are in contrast to the quantum yields for glasses, in which medium the emission intensity from $[Cr(NCS)_6]^{3-}$ has been reported to be two to three orders of magnitude greater than from any other complex.[5]

The intensities which we quote have been derived after correction for the wavenumber dependence of source intensity, instrumental transmission values, and detector response. In each case the energy of excitation was chosen to correspond with the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ absorption value. The observation of emission from diffusely reflecting powders using a small-angle viewing mode is critically dependent upon exclusion of stray excitation radiation. For our investigations we

Luminescence behaviour of tervalent chromium complexes

Complex	Literature values			Experimental values	
	Absorption ${}^4A_{2g} \leftarrow {}^4T_{2g}$ $\bar{\nu}_{max}$ (cm.$^{-1}$)	Emission (Low temperature glasses) ${}^4A_{2g} \leftarrow {}^2E_g$ $\bar{\nu}_{max}$ (cm.$^{-1}$)		Emission ${}^4A_{2g} \leftarrow {}^2E_g$ $\bar{\nu}_{max}$ (cm.$^{-1}$)	Relative intensity (±5%)
		Ref. 5	Ref. 4		
$K_3Cr(CN)_6$	26,000[a]	12,430	12,350	12,530	85
$Cr(en)_3Br_3$	21,850[a]	14,975	15,040	14,815	100
$Cr(NH_3)_6Cl_3$	21,550[a]	15,120	15,060	15,015	23
$Cr(biguanide)_3Cl_3$	20,700[b]	—	—	13,195	80
$K_3Cr(NCS)_6$	17,750[a]	12,850	12,890	12,920	98
Compare:—					
$Cr(acac)_3$	18,400[c]	12,838	12,800	—	—
$K_3Cr(ox)_3$	17,500[a]	14,392	—	—	—

[a] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon, Oxford, 1962; [b] R. H. Skabo, University of Tasmania, personal communication; [c] ref. 9.

have found an instrumental configuration comprising excitation and emission monochromators with filters to be best suited for this purpose.[11]

At this stage we have examined the temperature dependence of emission intensity over a limited range of temperatures and it would appear that the known inverse relationship[10] holds for the solids.

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