

Temperature and Solvent Dependence of Phosphorescence of Cr^{III} Complexes in Fluids

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Summary Phosphorescence from several Cr^{III} complexes in solutions at room temperature and above is observable and temperature and solvent dependence may be understood in terms of thermal repopulation of ⁴T states from the ²E state.

PHOSPHORESCENCE has been observed at room temperature from the Cr^{III}(en)₃³⁺ ion, (en = ethylenediamine),¹ in solution and from solid salts of Cr^{III} complexes.^{2,3} Analyses of such luminescence are useful in studies of the photoaquation reactions of Cr^{III} complexes in solution.^{1,4} We report the structure and solvent dependence of phosphorescence from Cr^{III} complexes at 5°–70 °C.

was examined in aqueous (and, solubility permitting, Me₂SO) solution. Contrary to earlier impressions,^{1–3} easily detected phosphorescence is common, but it is definitely not universal. There is no simple correlation with values of $E(^4T_2) - E(^2E)$ the difference in absorption spectral energies of the quartet and doublet states, except that all emitters have fairly large values of this difference. This parameter has been used as a guide to the relative positions of the doublet and the vibrationally equilibrated quartet.⁶ (It may be significant that non-emitting systems tend to be those of lower symmetry).

It has been suggested⁵ that the observation of solid-state room-temperature phosphorescence for [Cr(en)₃]Br₃² is associated with a heavy-atom effect, since the Br ion may

TABLE I

Phosphorescent emission from some Cr^{III} complexes in water at room temperature

Complex	λ excit. (nm)	λ emiss. (nm) ^a	Phosphorescence intensity ^b	$E(^4T_2) - E(^2E)$ 10 ⁻³ cm ⁻¹ ^c
Cr(Me ₂ SO) ₆ ³⁺	630	(690)		1.4
Cr(H ₂ O) ₆ ³⁺	579	(660)		2.1
Cr(ox) ₃ ³⁻	571	(696)		3.1
cis-Cr(en) ₂ Cl ₂ ⁺	532	(694)		4.4
Cr(NCS) ₆ ³⁻	565	769	v.w.	4.7
Cr(acac) ₃ ⁰	543	(772)		5.5
Cr(en) ₃ ox ⁺	495	(690)		5.7
Cr(NH ₃) ₅ H ₂ O ³⁺	481	667	v.w.	5.8
Cr(NH ₃) ₅ SCN ²⁺	487	686	v.w.	5.9
trans-Cr(NH ₃) ₂ (SCN) ₄ ⁻	519	750	w.	6.0
Cr(MeNH ₂) ₆ ³⁺	475	665	m.s.	6.0
Cr(NH ₃) ₆ ³⁺	464	654	s.	6.3
Cr(phen) ₃ ox ⁺	502	745	v.w.	6.3
trans-Cr(en) ₂ (SCN) ₂ ⁺	497	727	m.s.	6.4
Cr(en) ₃ ³⁺	458	670	s.	6.9
Cr(biguanide) ₃ ³⁺	483	(758)		7.5
Cr(bipy) ₃ ³⁺	455	727	v.s.	8.3
Cr(phen) ₃ ³⁺	420	730	v.s.	10.1

ox = oxalate, acac = acetylacetonate, phen = phenanthroline, bipy = 2,2'-bipyridyl.

^a For complexes not observed to phosphoresce, the values in parentheses are the doublet absorption wavelengths. ^b v.w. very weak; w. weak; m.s. moderately strong; s. strong; v.s. very strong. ^c $E(^4T_2)$ is the energy of the 1st spin-allowed quartet absorption (not emission) band. $E(^2E)$ is the energy of the doublet state emission band.

We used an Aminco-Bowman spectrofluorimeter equipped with an R446S phototube and a thermostatted cell chamber for 1.00 cm cells. The excitation spectrum conformed qualitatively to the absorption spectrum in the spin-allowed ligand-field bands, and results are reported for irradiation at the maximum of the lower spin-allowed ligand-field band ($^4T_{2g} \leftarrow ^4A_{2g}$ in O_h symmetry). Emission maxima appear at wavelengths corresponding to the spin-forbidden doublet absorption band ($^2E_g \leftarrow ^4A_{2g}$ in O_h symmetry). On this basis, they are assigned as doublet phosphorescence in agreement with solid-state and low-temperature studies.⁵ Relative intensities were estimated from the integrated emission band areas. Concentrations were chosen in a range where intensities were linear in concentration.

Table I gives a qualitative summary of systems exhibiting room temperature solution phosphorescence. Emission

facilitate quartet-doublet intersystem crossing, but we found that the phosphorescence intensities of aqueous solutions of Cr(en)₃³⁺ and Cr(NH₃)₆³⁺ were unaffected by the addition of heavy anions (or cations).

Analysis of low temperature spectra in crystals and glasses⁵ indicates that the dominant temperature-dependent process is the thermal repopulation of ⁴T from ²E. (Phosphorescence decreases with increasing temperature, and in some cases fluorescence intensity increases.⁷ We observe a similar temperature dependence of relative intensity of phosphorescence from Cr^{III} complexes which fits accurately (s.d. <3%) to a single activation energy for each compound in each solvent (see Table 2).

If the part of photosubstitution of Cr(NH₃)₂(NCS)₄⁻⁸ which can be quenched by a doublet quenching reagent proceeds *via* thermal repopulation of the quartet, then data like those in Table 2 predict the solvent dependence and

apparent activation energy of that photosubstitution pathway. Also the data in Table 2 help to place the quartet state on an energy scale and to reveal its response to

solvent changes, thus elucidating the pathway of electronic relaxation in that state, which, because of the unobservability of fluorescence, cannot be examined directly.

TABLE 2

Temperature dependence of the phosphorescence intensity of some Cr^{III} complexes in various solvents

Complex	$E_a(10^{-3} \text{ cm}^{-1})^a$		DMF ^b	Me ₂ SO
	D ₂ O	H ₂ O		
Cr(NH ₃) ₆ ³⁺	3.79 ± 0.1	3.65 ± 0.1	4.46 ± 0.1	4.91 ± 0.1
Cr(MeNH ₂) ₆ ³⁺		3.26 ± 0.1	4.14 ± 0.1	
Cr(en) ₃ ³⁺		3.68 ± 0.1	3.75 ± 0.1	4.07 ± 0.1
Cr(bipy) ₃ ³⁺		2.63 ± 0.1 ^c	2.39 ± 0.1	2.77 ± 0.1
Cr(phen) ₃ ³⁺		1.58 ± 0.1		
<i>trans</i> -Cr(en) ₂ (SCN) ₂ ⁺ ..		2.14 ± 0.1		2.98 ± 0.2

^a The standard deviations obtained from least-squares analyses of log intensity *versus* 1/T data are quoted as a measure of the accuracy of the E_a values. ^b DMF = dimethylformamide. ^c Corresponding value in 0.40M-HCl is $E_a = 2700 \pm 100 \text{ cm}^{-1}$.

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