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The Effect of Environmental Rigidity on Nonradiative Decay in Chromium(III) Amines

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Abstract

The lifetimes of $Cr(NH_3)_6^{3+}$ and the Cr(cyclam)-$(NH_3)_2^{+}$ complexes, both protiated and deuterated, have been recorded in aqueous polyalcoholic and DMSO solutions in the temperature range that includes the change from a rigid glass to a fluid. A small but distinct lifetime reduction is associated with increased solvent mobility in the protiated species but not in the deuterated complex. This is interpreted to indicate that increasing anharmonicity in accepting modes enhances the nonradiative rates.

Introduction

Interest in the effect of environmental mobility on molecular emission has been high ever since Lewis and Kasha recognized that the phosphorescence intensity was profoundly diminished when the solvent rigidity was lost [1]. Photophysical studies of metal complexes as a function of temperature often encompass a range in which the host solvent is transformed from a rigid to a fluid medium. An abrupt change in lifetime or emission spectrum is frequently observed in a small temperature interval which coincides with a palpable decrease in rigidity. The thermal reduction of the tris-acetylacetonatochromium(III) lifetime in a series of alcohols was ascribed to the decreased solvent viscosity [2]. Alcohol/water and alcohol/ether mixed solvents exhibit viscosity changes of four orders of magnitude in a 10°–15° interval at low temperatures [3]. This phenomenon is loosely called solvent 'melting', although it corresponds neither to melting of a crystal nor to a glass transition. If the photophysical properties of a molecule depend upon viscosity, then these properties will change abruptly with temperature in the range where the thermal gradient of viscosity is large. Barigelletti *et al.* have studied the effect of temperature and solvent rigidity on the emission of $Ru(bpy)_3^{2+}$ and several derivatives [4]. They found a small thermal enhancement of nonradiative processes in rigid media, followed by a steep increase in the relaxation rate in a narrow temperature interval (20°–30°) and a return to the small temperature dependence when the solvent becomes fluid. The activation energies for the thermal decay were the same in both the rigid and fluid regions, suggesting that the only effect of solvent melting was the introduction of a constant contribution to the nonradiative decay.

Ferguson and Krausz have ascribed the changes in the $Ru(bpy)_3^{3+}$ emission in the solvent melting region to two processes: the change from a delocalized to a localized charge transfer state and relaxation of solvent dipoles [5]. $^2E \rightarrow {}^4A_2$ emission in Cr(III) complexes is metal localized and the question of ligand localized excitation does not arise. There is evidence for a viscosity mediated decay channel in alcohol/H_2O solutions of $Cr(NH_3)_6^{3+}$, but an abrupt break of the sort observed in $Ru(bpy)_3^{2+}$ would be obscured by a second decay channel with a larger activation energy [6]. Since the major thermal quenching of *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ occurs at much higher temperatures than in $Cr(NH_3)_6^{3+}$ [7], any break associated with solvent melting should be detectable in solutions of the cyclam complex. We now present evidence for the existence of a small, but definite, enhancement of nonradiative decay in CrN_6 complexes brought about by increasing solvent motions.

Experimental

Solvents were: EGW, ethylene glycol/H_2O (2:1 *v*/*v*); GLW, glycerol/H_2O (9:1 *v*/*v*), DMSO/H_2O and DMSO/D_2O (1:1 *v*/*v*). *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ and *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ were supplied by O. Mønsted. The complexes were deuterated by letting the D_2O solutions of the protiated species stand at room temperature for $1\frac{1}{2}$–2 h prior to mixing with an equal volume of DMSO.

Excitation was at 337 nm with an N_2 laser. The lifetimes were determined as described elsewhere [8]. The decay profiles were collected until the emission fell to 10% of the initial value and were digitized and averaged over 1024 pulses. The degree of exponentiality was estimated by comparing the

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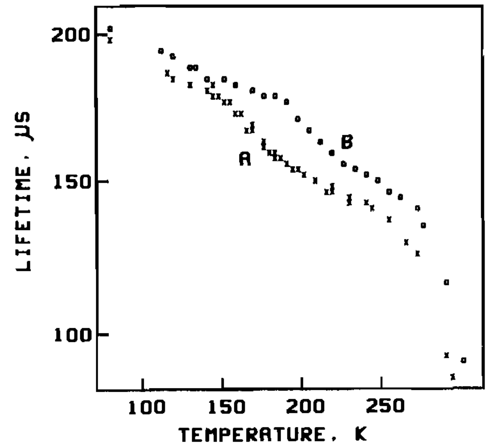

Fig. 1. The temperature dependence of the *trans*-Cr(cyclam)-$(NH_3)_2^{3+}$ lifetime in alcohol–water solvents: A, EGW; B, GLW.

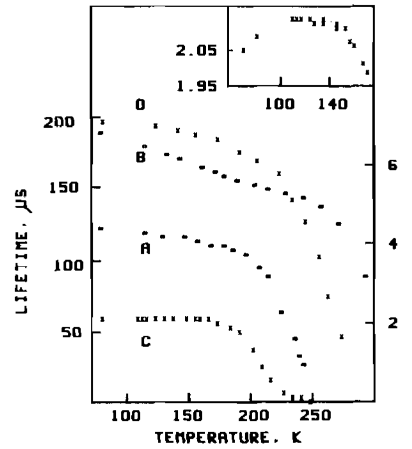

Fig. 2. The temperature dependence of lifetimes: *cis*- (A) and *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ (B) in $DMSO/H_2O$ (left ordinate scale); *cis*- (C) and *trans*-Cr(D-cyclam)$(ND_3)_2^{3+}$ (D) in $DMSO/D_2O$ (right ordinate scale). Inset: *cis*-Cr(D-cyclam)-$(ND_3)_2^{3+}$ in $DMSO/D_2O$, expanded ordinate scale.

lifetimes in the first and last quarter of the decay curve. If the ratio of these lifetimes is 0.95–1.05 the decays are designated as exponential. In most cases the deviation of the ratio from unity is much smaller. Except where indicated otherwise, all the decays are exponential by this criterion and by visual examination of semi-logarithmic plots of the decay profiles.

The 77 K measurements were made by rapid immersion of the sample into liquid N_2. Temperature control above 77 K was obtained by directing a cold stream of N_2 gas into the dewar in which the sample was suspended. Temperatures were monitored with Cu-constantan thermocouples inserted into the sample and near the outer surface of the cuvette. Thermal equilibrium was achieved throughout the entire sample. Relative temperatures are reliable to 1°. Temperatures as low as 63 K were achieved by pumping on liquid N_2. Normally the lifetimes were recorded as a function of increasing temperature. In several cases, as specified, the record was obtained as the temperature was decreased.

Results

trans-Cr(cyclam)$(NH_3)_2^{3+}$

The effect of temperature on the lifetime of this complex in EGW (Fig. 1) provides the basis for describing the thermal behavior of all the complexes. The exponentiality is very good in this system. Below 150 K the lifetime decreases slowly with temperature. From 180–250 K the same slow thermally enhanced decrease is again observed. Between 150 and 180 K the lifetime decreases steeply. Although the lifetime drop is small, this feature is reproducible. Exactly the same curve is obtained when the liquid is cooled and there was no evidence of hysteresis. Above 250 K a rapid lifetime drop prevails. The lifetime reduction near 160 K is less pronounced in $DMSO/H_2O$ (Fig. 2) but in other respects the behavior is similar to that in EGW. The break due to increased fluidity appears at 190 K in the more viscous GLW (Fig. 1). The decays are slightly non-exponential in GLW.

trans-Cr(D-cyclam)$(ND_3)_2^{3+}$

The 77 K lifetime of this deuterated species in $DMSO/D_2O$ is 7.1 ms, the longest reported for any CrN_6 complex. This value is so much larger than the lifetime of the protiated complex that incomplete deuteration would not affect the results. The lifetime decreases smoothly with temperature and there is no hint of any slope discontinuity (Fig. 2).

cis-Cr(cyclam)$(NH_3)_2^{3+}$

The 150 K breaks are less pronounced in both EGW and $DMSO/H_2O$ than are the corresponding effects in the *trans* counterpart (Figs. 2 and 3).

cis-Cr(D-cyclam)$(ND_3)_2^{3+}$

As in the case of the deuterated *trans* complex there is no break near 150 K (Fig. 2). In contrast to the behavior of the *trans* complex, the lifetime does not exhibit a monotonic decrease with temperature. Instead, there is a maximum near 120 K (Fig. 2 inset).

$Cr(NH_3)_6^{3+}$

The slope discontinuity at 150 K is again present in EGW solution (Fig. 3). The high temperature lifetime does not decrease as precipitously in $Cr(NH_3)_6^{3+}$ as in *cis*-Cr(cyclam)$(NH_3)_2^{3+}$.

It must be emphasized that the data were sufficiently precise to justify the above statements, even when the effects are small.

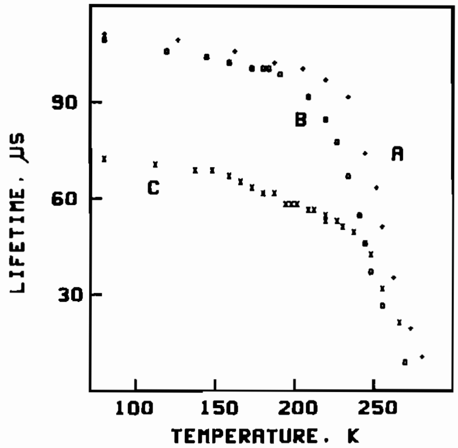

Fig. 3. The temperature dependence of lifetimes: A, *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ in GLW; B, *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ in EGW; C, $Cr(NH_3)_6^{3+}$ in EGW.

Discussion

At low temperatures the radiative rate in protiated CrN_6 complexes is small compared to the nonradiative rate, while in the deuterated analogs the radiative rate dominates. Consequently, the observation of an abrupt decrease in the decay time associated with increasing solvent mobility in all three protiated species, coupled with the absence of such an effect in the deuterated complexes, clearly indicates that only the nonradiative rate is influenced by environmental mobility. The same conclusion pertains to $Ru(bpy)_3^{2+}$ [4].

The time required to change the temperature exceeded several minutes and the absence of hysteresis demonstrates that the solvent envelopes correspond to equilibrium assemblies with respect to the relevant degrees of freedom at each temperature. Parenthetically, there was no change in the lifetime when the glass was maintained at 77 K for more than one hour. This rules out slow relaxation processes of the type reported at 4 K for $Ru(bpy)_3^{3+}$ [9].

The behavior of the CrN_6^{3+} complexes is quite different from that of $Ru(bpy)_3^{2+}$ during the rigid–fluid transition. In the first place the time-resolved $Ru(bpy)_3^{2+}$ spectra shift to the red with delay time at some temperatures and the overall emission spectrum is redshifted as the viscosity is reduced in a particular temperature range [10]. Secondly, the $Ru(bpy)_3^{3+}$ excited state decays are exponential in both the rigid glass and very fluid media but non-exponential in the transition region where the glass softens [5]. Both of these observations implicate solvent motions that compete with excited state decay. In contrast, the CrN_6^{3+} decays remain exponential and the emission spectra are independent of delay time and viscosity over the entire temperature range. The invariance of the ^2E energy rules out a reduction of the energy gap as the origin of the decay rate change [11]. In general, ground and excited state geometries are different, but in the $^2E \rightarrow {}^4A_2$ transition both states are derived from the t_2^3 configuration and the equilibrium position is hardly affected by excitation. Furthermore, the solute species are nonpolar. This means that neither solvent rotation nor translation will stabilize the excited state relative to the Franck–Condon state, in contrast to the situation where the solute is polar or there is a geometry change upon excitation. Consequently, the emission spectrum is not dependent upon solvent mobility and the excited state does not set the time scale for effective solvent motions.

In EGW solutions of *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ the lifetime decrease associated with the 150 K break is approximately 10%. The corresponding change in $Ru(bpy)_3^{2+}$ and derivatives is 30–80%. Bargelletti *et al.* suggested that the decreased nonradiative rate in rigid media is due to the change of the potential energy curve which leads to a 'freezing' of skeletal vibrations that function as promoting modes [4]. According to the propensity rule [12] the radiative and nonradiative rates should be similarly affected by variations in promoting mode efficiencies. Yet, there is no slope discontinuity in deuterated *cis*- and *trans*-Cr(D-cyclam)$(ND_3)_2^{3+}$ where the decays are essentially radiative below 150 K. An alternative explanation focuses on the accepting modes. The effect of solvent mobility is to increase the anharmonicity of the accepting vibrations [13, 14], which in turn increases the accepting mode Franck–Condon factors. Since many quanta of the accepting modes are excited, the Franck–Condon factors should be very sensitive to small changes in the ground state anharmonicity. Although the Dellinger and Kasha description is couched in kinetic language, it is difficult to assess the magnitude of solvent motions needed for the anharmonicity increase. This situation is analogous to the ill-defined boundary between librations and rotational relaxation in liquids [15]. No time scale for potential surface changes can be established, but the excited state lifetime is not the relevant parameter.

The slope discontinuity that begins at about 190 K in the GLW solution of *trans*-Cr(cyclam)$(NH_3)_2^{3+}$ is the analog of the 150 K break in EGW.

The ^2E level is split in non-cubic fields. This splitting is less than the line widths (5–10 cm^{-1}) in crystals containing $Cr(NH_3)_6^{3+}$ [16], but exceeds 100 cm^{-1} in acidopentamminechromium(III) complexes [17]. The O–O transition is relatively weak in the *trans* complex and the smaller lifetimes in the *cis* complexes are the result of distortion from centrosymmetry that is found in *cis* cyclam complexes [11]. The distortion affects the radiative rate more than the nonradiative rate as evidenced by the larger difference in the low temperature lifetimes in the deuterated isomer pair than in the protiated analogs. The maximum in the lifetime plot of *cis*-Cr(D-cyclam)$(ND_3)_2^{3+}$ in the rigid glass region indicates that radiative rates from the ^{2}E components are different and that the population of these components changes appreciably in the 63–150 K interval. An analogous behavior prevails in ruby [18]. In contrast, the lifetime of *trans*-Cr(D-cyclam)$(ND_3)_2^{3+}$ exhibits a monotonic decrease with temperature. This would be consistent with the smaller ^{2}E splitting expected in the *trans* complex where there is little skeletal distortion.

Since the lifetimes in the protiated CrN_6 complexes are mainly nonradiative, the absence of a maximum in the *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ plot indicates that the nonradiative decay rates are nearly the same for both of the ^{2}E components. If this result is general, the small thermally induced decreases in lifetime commonly observed in rigid solutions of Cr(III) complexes are due to increases in nonradiative rates rather than to changing populations.

$\tau^{-1} - \tau_0^{-1}$ exhibits an Arrhenius dependence above 190 K for *cis*-Cr(D-cyclam)$(ND_3)_2^{3+}$ in DMSO/D_2O with $E_a = 3400$ cm^{-1}. The corresponding Arrhenius plot for *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ in DMSO/H_2O is biphasic with $E_a = 2780$ and 150 cm^{-1}. The photolability of *cis*-Cr(cyclam)$(NH_3)_2^{3+}$ complexes in water at 20 °C compared to the photoinertness of the *trans* complex under the same conditions [7] suggests that the 2780 cm^{-1} process may be a photoreaction. The activation energy for thermally enhanced nonradiative decay is then 150 cm^{-1}.

Acknowledgements

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