Photoselection Studies of Transition Metal Complexes.
IV. The Emission Intensity Mechanism for Cr(III)—Sulfur Complexes

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Abstract

Luminescence spectra and photoselection spectra have been measured for some Cr(III) complexes having molecular D_3 symmetry including $Cr(exan)_3$, $Cr(dmtc)_3$, and $Cr(acac)_3$. The photoselection data is consistent with an intensity mechanism for emission involving a pure spin—orbit mixing of the quartet and doublet manifold; however, the results are not conclusive. The photoselection spectra for the Cr-$(dmtc)_3$ complex, for which an unusual hybrid fluorescence—phosphorescence has been observed, implies that this emission is occurring from a single potential surface rather than an overlapped dual emission resulting from separate quartet and doublet excited states.

Introduction

The emission photoselection method has proved useful in assessing emission intensity mechanisms for a variety of organics including nitrogen heterocycles [1, 2]. For transition metal complexes, the technique has been utilized to verify the presence of multiple state emission in d^6 metal—sulfur complexes [3], to characterize the emitting state of $Ru(bpy)_3^{2+}$ as a localized state [4, 5], to identify the emitting state for d^8 metal complexes [6, 7] and most recently, for the determination of the intensity mechanism of emission for metal localized Cr(III) complexes [8].

The photophysics and photochemistry of Cr(III) complexes has been extensively explored, in large part due to the ease of synthesis of a great range of Cr(III) complexes. The first attempts to systemize the results of photochemistry dealt with the photochemical substitution reactions of Cr(III) complexes [9, 10]. From these empirical correlations, a number of models have evolved [11–16] attempting to rationalize the photochemistry in terms of orbital electron densities in excited states. No comparable amount of theoretical activity has occurred to rationalize the photophysical processes in Cr(III)

complexes, although an attempt has been made by Robbins and Thomson [17] to rationalize the radiationless deactivation of Cr(III)—beta-diketone complexes in terms of the Jortner weak coupled system approach. This emphasis upon vibronic interaction in the deactivation of the excited state is the focus of an effort by Hollebone, Langford and Serpone [18] but such an emphasis upon the vibronic interaction has not been, to date, fully integrated into the rationale of the deactivation of the excited states.

Among the Cr(III) complexes, narrow, structured phosphorescence (spin forbidden process) occurring from approximately vertical surfaces [19] is the common form of emission with the broad structureless fluorescence (spin allowed process) occurring for only a few complexes [20]. In one case, the tris diethyldithiocarbamate complex of Cr(III), a unique hybrid fluorescence—phosphorescence emission occurs. This emission exhibits a band width and Stokes shift intermediate between that of a pure phosphorescence and a pure fluorescence, apparently due to the near degeneracy of the lowest quartet and doublet states. Such a degeneracy suggests that the spin, S may not be a valid quantum number to describe these states, therefore that these systems may in this sense resemble the heavier metal d^6 complexes previously examined [4, 5]. Alternatively, the unusual emission spectral appearance could derive from the overlap of a multiple emission, both a fluorescence and phosphorescence with the net appearance of the emission as observed. The latter such occurrence might be expected to manifest itself in unusual emission polarization spectra. To answer this question and to attempt to assess the effect of the potential surface displacement upon vibronic coupling, the photoselection spectra of the structurally related tris ethylxanthate $(Cr(exan)_3)$ and tris dimethyldithiocarbamate $(Cr(dmtc)_3)$ complexes of Cr(III) have been determined and are reported here. The tris acetylacetone $(Cr(acac)_3)$ complex of Cr(III) has been utilized as a reference material since this complex and the two sulfur complexes have near isoenergetic emission.
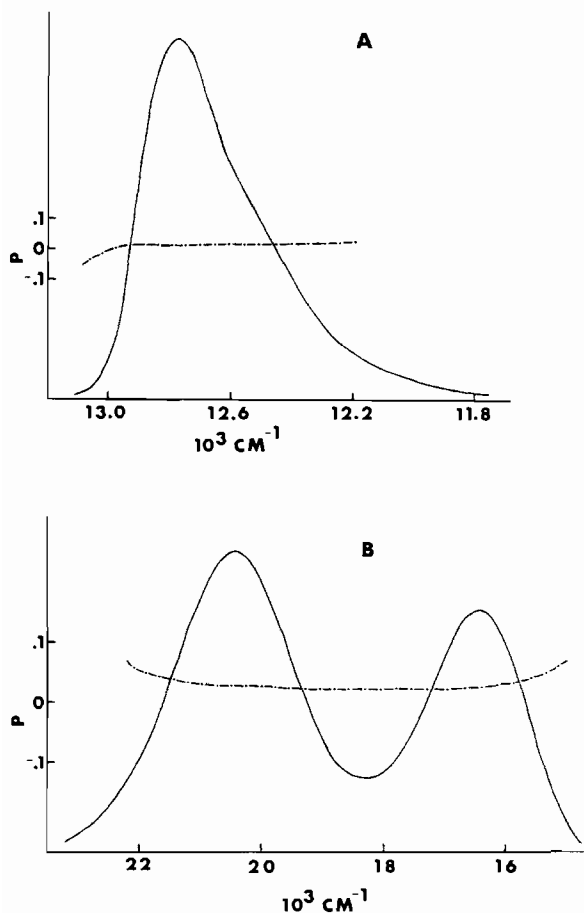
Fig. 1. Cr(exan)₃ spectra. A) Emission and emission polarization spectra (80 K) for 20,408 cm⁻¹ (490 nm) excitation. B) Low temperature absorption spectrum (83 K) and excitation polarization spectrum (80 K) for 12,771 cm⁻¹ (783 nm) emission.

Experimental

Tris(ethylxanthanato)chromium(III), Cr(exan)₃, tris(dimethyldithiocarbamato)chromium(III), Cr-(dmtc)₃ and tris(acetylacetonato)chromium(III), Cr-(acac)₃ were prepared previously in this laboratory [21]. The three complexes were recrystallized from hot alcohol solutions and the Cr(dmtc)₃ complex was further purified by sublimation. After purification absorption and emission spectra were found to match those previously reported [21] and emission spectra were found to be independent of excitation wavelength.

Instrumentation

A low temperature cryostat made in this lab was used with a Cary 14 spectrophotometer to obtain the low temperature absorption spectra. The base line offset was not corrected and only relative intensities are shown. Emission and photo-
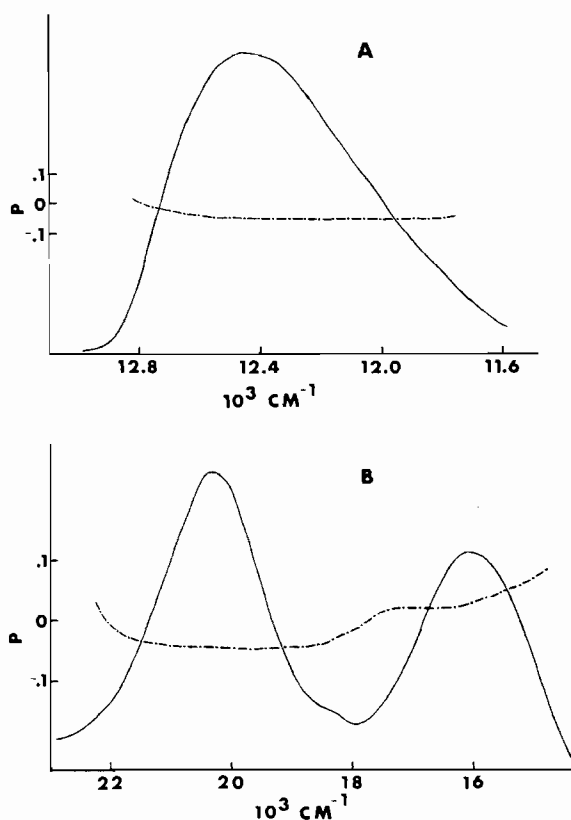

Fig. 2. Cr(dmtc)₃ spectra. A) Emission and emission polarization spectra (80 K) for 20,000 cm⁻¹ (500 nm) excitation. B) Low temperature absorption spectrum (83 K) and excitation polarization spectrum (80 K) for 12,346 cm⁻¹ (810 nm) emission.

selection spectra were obtained for samples frozen in glassy solvents using a computer controlled instrument that has been described previously [22]. For this work it was necessary to replace the emission polarizer with a glan Thompson prism since the polarizers begin to transmit unpolarized light at wavelengths greater than 750 nm. Excitation photoselection spectra were obtained while monitoring the first strong emission peak. Standard deviations of the polarization value (P) were no larger than 0.03 and were usually less than 0.02 unless otherwise stated.

Results

The emission spectra, absorption spectra, emission polarization and excitation polarization spectra for Cr(exan)₃ and Cr(dmtc)₃ are shown in Figs. 1 and 2. A D₃ symmetry energy level diagram appropriate to the Cr–S chelate complexes is shown in Fig. 3.

The 80 K luminescence spectra of the sulfur complexes are identical to those previously reported
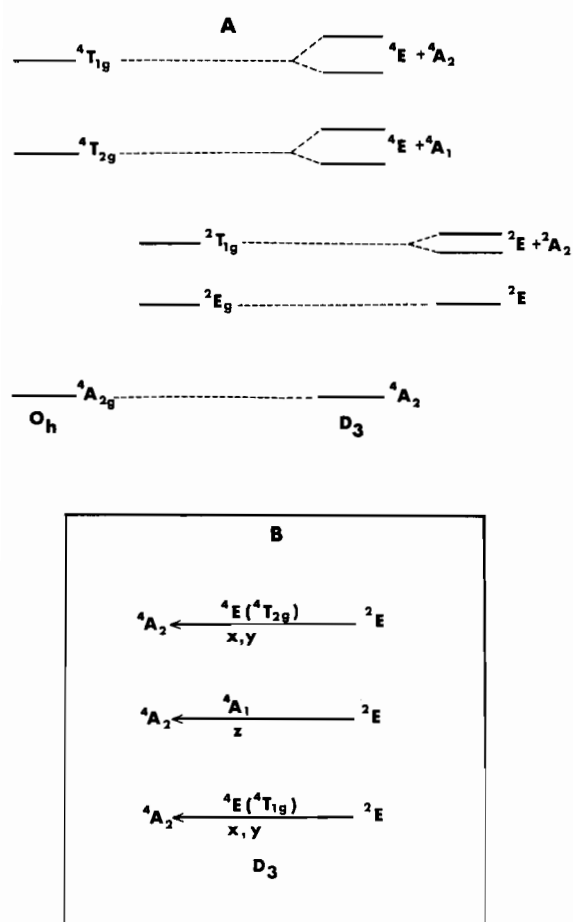
Fig. 3. A) D_3 – Energy level diagram as derived from O_h.
B) D_3 – Results of spin–orbit coupling.

[21] with a typical narrow band phosphorescence observed for the Cr(exan)$_3$ complex and a broader structureless emission occurring for the Cr(dmtc)$_3$ complex. The emission band observed for the Cr-(acac)$_3$ is as reported [23] and can be readily identified as 'phosphorescence'. The emission vibrational structure observed is less prominent in glassy solution than that measured for the D_3 Cr(en)$_3$$^{3+}$ complex. Similarly, the emission polarization spectra of these sulfur chelate complexes does not evidence vibrational structure as was observed [8] for the Cr(en)$_3$$^{3+}$ and Cr(bpy)$_3$$^{3+}$ complexes. The Cr(acac)$_3$ emission polarization spectra does show some vibrational structure; however, it is almost within the experimental error and is not conclusive.

The excitation polarization spectra of these sulfur chelate complexes differ. The excitation polarization of the Cr(exan)$_3$ complex is near zero (Fig. 1) and constant over the entire visible region while the excitation polarization of the Cr(dmtc)$_3$ complex is more like that of the Cr(en)$_3$$^{3+}$ complex changing from slightly negative values across the high energy

($^4T_1$) absorption band to slightly positive values across the lower energy ($^4T_2$) absorption band (Fig. 2).

It should be emphasized that interpretation of the polarization data is based on the general shapes of the polarization spectra, which are reproducible, and not on absolute polarization values.

Discussion

Two aspects of the polarization spectra for the sulfur chelates are unique and require discussion:

(a) The absence of vibrational structure in the emission polarization for both complexes and

(b) the constant near zero excitation polarization of the Cr(exan)$_3$ complex through the entire visible region.

The first observation may have one of two alternative origins, *i.e.*,

(1) the near zero polarization measured for these systems tends to obliterate any real oscillations in the polarization value, or

(2) the absence of polarization structure in the emission does indicate that a pure spin–orbit mechanism dominates any second order spin-vibronic mechanism that occurs.

The Cr(acac)$_3$ data were obtained with the goal of distinguishing between the two rationale. The Cr(acac)$_3$ complex emits at approximately the same energy as the sulfur chelates but the energy gap between the emitting doublet and the quartet manifolds (as estimated by the difference between emission and absorption band maxima) is much larger for Cr(acac)$_3$ than for the sulfur chelates, consequently the first order spin–orbital mixing of quartet into doublet states should be much larger for the sulfur chelates than for the Cr(acac)$_3$. The absence of any vibrational structure in the emission polarization of these sulfur complexes is consistent with such an interpretation. However, the minimal oscillation of the emission polarization for the Cr(acac)$_3$ complex where the energy gap is of similar magnitude to the Cr(en)$_3$$^{3+}$ and Cr(bpy)$_3$$^{3+}$ (for which a vibronic pattern could be discerned in the polarization) makes uncertain the origin of this lack of vibronic interaction.

The second result, the constant near zero polarization of the Cr(exan)$_3$, is quite unusual since the emission for this complex was thought to be a normal phosphorescence. Therefore a polarization like that of the Cr(en)$_3$$^{3+}$ and the Cr(bpy)$_3$$^{3+}$ complexes [8] was expected. Since the ^2E emitting state can couple to all of the allowed quartets an emission oscillator with components in the (x, y) and z directions is expected. A near zero value for the polarization would be expected if the magnitude of (x, y) and z emission components is nearly the same. However,
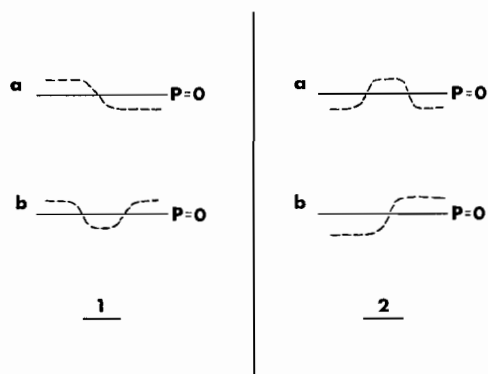
Fig. 4. General shapes of the polarization spectrum for D_3 symmetry. 1) predominant (x, y) emission. a) $^4A_1$ lowest spin allowed state; b) ^4E lowest spin allowed state. 2) predominant z emission. a) ^4E lowest spin allowed state; b) $^4A_1$ lowest spin allowed state.

for the higher energy quartet absorption only, the transition to the ^4E component is symmetry allowed while that to the $^4A_2$ is forbidden in first order. Thus, the polarization is expected to change across the two quartet visible absorption bands. This is the situation that does occur for the $Cr(en)_3^{3+}$, $Cr(bpy)_3^{3+}$ [8] and $Cr(dmtc)_3$ complexes. Thus, the $Cr(exan)_3$ complex with an apparently normal phosphorescence does exhibit an anomalous excitation polarization whereas the $Cr(dmtc)_3$ for which a unique phosphorescence has been identified does produce a 'normal' excitation polarization profile.

At least two explanations of this behaviour for the $Cr(exan)_3$ complex are possible.

(1) The ^4E dominates the emission oscillator implying that the $^4A_1$ (of the $^4T_2$ state) contributes a negligible amount to the oscillator or

(2) The overlapping of the absorption bands leads to a flat polarization across the absorption bands.

The first rationale is difficult to accept since single crystal polarization spectra [24] indicate that the $^4A_1$ component is approximately as intense as the ^4E component. The second alternative can be understood by reference to Fig. 4 where the four general shapes of the polarization are described. Curves 1b and 2a would be obtained respectively for a dominant (x, y) emission oscillator, lowest ^4E state (of $^4T_2$) and for dominant z emission oscillator, lowest ^4E (of $^4T_2$), respectively. In the limit of overlapping bands and near spherical emission oscillator the polarization dispersion would be flat across the two quartet bands as occurs with the case of 1b having slightly positive values and case 2a with slightly negative values. Therefore the positive values of the polarization imply that case 1b is the appropriate case.

The unstructured emission photoselection spectrum for the $Cr(dmtc)_3$ complex implies that this

emission occurs from a single potential surface and is not a dual emission resulting from separate overlapping quartet and doublet excited states since such an occurrence would necessarily show a non zero slope in the polarization across the emission band. The difference in the behavior of the polarization of the two sulfur complexes does imply that the emission oscillator for $Cr(exan)_3$ is dominant (x, y) while that for $Cr(dmtc)_3$ is dominant z. This can be interpreted as indicating that the lowest energy doublet state, for the two sulfur chelates, couples differently to the two lowest lying ^4E and $^4A_1$ states (of $^4T_2$). This might be expected since for $Cr(dmtc)_3$ the emitting doublet state is at about the same energy or higher than the lowest quartet states, whereas for $Cr(exan)_3$ the emitting doublet state is lower in energy than the lowest lying quartet states. As a result spin—orbit coupling will be stronger for $Cr(dmtc)_3$ and might lead to an emitting state in which the spin quantum number is not very significant. Such an explanation has been suggested by Kane-Maguire and coworkers to explain intersystem crossing efficiencies for $Cr(en)_3^{3+}$ in room temperature solution [25]. Attempts to rationalize these points must await verification of the low energy quartet states by single crystal polarization.

Conclusion

The photoselection spectra for the $Cr(dmtc)_3$ complex, for which an unusual hybrid fluorescence—phosphorescence has been suggested as the origin of the emission, is similar to the photoselection spectra of the other two normal D_3 phosphorescent emitters. Thus the best interpretation of the unusual band shape of the emission is that the emission is occurring from a single potential surface in which the spin quantum number is not valid, rather than the alternative interpretation of the emission as resulting from the overlap of simultaneous phosphorescence and fluorescence. These photoselection spectra and those previously reported [8] do permit recognition of the fact that the photoselection method produces greater resolution for lower symmetry molecule systems than for higher symmetry systems since the range of polarization values permitted to, for example, C_{2v} systems is sufficient to permit observation of modulating vibronic effects whereas that permitted to, for example, D_3 systems is less both due to overlapping bands and due to the lesser polarization values permitted by theory. Thus, the fact that the photoselection spectra for the sulfur chelates of Cr(III) do not show vibronic structure in the emission polarization, is consistent with a pure spin—orbit mixing of the quartet and doublet manifolds

but cannot, for the reasons above be used as the sole proof of such a mechanism.

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