Contribution from the Department of Chemistry,
University of Illinois, Urbana, Illinois 61801

Examination of Photophysics in Chromium(III) Complexes by Laser-Excited Luminescence

W. M. WATSON, YU WANG, JAMES T. YARDLEY,*[1] and GALEN D. STUCKY*

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Time-resolved, wavelength-resolved observations of the luminescence of several chromium(III) coordination complexes after pulsed laser excitation were undertaken to obtain information about nonradiative transitions between excited electronic states. The complexes tris(acetylacetonato)chromium(III) and hexacyanochromate(III) were excited into the metal-localized $^4T_{2g}$ or $^4T_{1g}$ states by various tunable dye laser configurations or into ligand-localized singlet states by a nitrogen laser. In each case, only $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence could be observed. The rise times of the emission and, hence, the rate of population of the ^2E_g state were shorter than the time resolution of the experiments. The rate constant for $^4T_{2g} \rightsquigarrow {}^2E_g$ intersystem crossing in the first compound was estimated to be greater than 10^5 sec^{-1}. The complexes hexaureachromate(III) and hexaantipyrenechromate(III) were excited into the metal-localized $^4T_{2g}$ or $^4T_{1g}$ states and appeared to luminesce from both the $^4T_{2g}$ and ^2E_g states. These emissions displayed different time behaviors; both were nonexponential decays. The time behavior of both emissions, the relative luminescence quantum yields, and certain features of the steady-state emission spectra were clearly concentration dependent.

I. Introduction

In metal complexes, photoinitiated processes often involve the excitation of ligand or metal localized excited states higher in energy than the lowest-energy excited states. The ultimate fate of the excited molecules may be determined to a large degree by the subsequent nonradiative relaxation into other excited states. We report here attempts to examine the nonradiative decay paths *between* excited states in several Cr(III) complexes with the aid of a pulsed tunable dye laser. Additional work on some rare earth complexes will be reported.[2]

Figure 1 outlines the electronic energy level structure for a typical Cr(III) complex. In particular, it will be noted that the relative energies of the ^2E_g and $^4T_{2g}$ excited states are strongly dependent upon ligand field strength. For the complexes examined here, the ^2E_g state lies at lower or comparable energy to the $^4T_{2g}$. A relatively strong radiative transition connects the $^4A_{2g}$ ground state to the $^4T_{2g}$ state, while a radiative transition to the ^2E_g level is extremely weak and transition to the $^4T_{1g}$ is strongly forbidden. Of course, ligand-centered singlet–singlet transitions (Figure 1) may be strongly allowed also. Previous examinations of photophysical processes in Cr(III) have been reviewed recently by Fleischauer and Fleischauer[3a] and by Forster.[3b]

For strong-field ligands, in which the ^2E_g level lies lowest in energy, excitation into metal-localized or ligand-localized bands leads primarily to $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence. Recently, the observation of *fluorescent* decay $^4T_{2g} \rightarrow {}^4A_{2g}$ in several such systems has been reported,[3c] and values have been given for the fluorescence decay times. These results have been contradicted by Yardley and Beattie[4a] and by Castelli and Forster.[4b] Here we report further investigations concerning intramolecular electronic energy-transfer processes in such complexes.

In some complexes of lower ligand field strength, the ^2E_g and $^4T_{2g}$ states are of nearly the same energy. Steady-state emission spectra for a number of these complexes have been reported and interpreted in terms of *both* ^2E_g *and* $^4T_{2g}$ emission.[3a,3b,4c] Time-resolved and wavelength-resolved luminescence decay measurements are reported here for two such complexes.

II. Experimental Section

$[Cr(ur)_6]Cl_3$ precipitated from an ethanolic solution of $CrCl_3{\cdot}6H_2O$ and urea and was recrystallized from ethanol. $[Cr(antip)_6](NO_3)_3$ was prepared from an ethanolic solution of $[Cr(H_2O)_6](NO_3)_3$ and antipyrene by slowly evaporating the solvent until a viscous green tar remained and was recrystallized twice from ethanol–tetrahydrofuran. $K_3[Cr(CN)_6]$ and $[Cr(acac)_3]$ were obtained from Dr. J. C. Bailar and Dr. J. K. Beattie, respectively.

The complexes were dissolved in appropriate glass-forming solvents, including (equal parts by volume) diethyl ether–2-methylbutane–ethanol (EPA), methanol–ethanol (ME), methanol–ethanol–1,2-ethanediol–water (MEGW). Approximately 1-ml samples were filtered through fritted glass and were introduced into 18-mm Pyrex ampoules. These were repeatedly degassed by freeze (77°K)–pump (10^{-6} Torr)–thaw cycles and sealed off. During luminescence experiments, these ampoules were completely immersed in liquid nitrogen within the sample dewar. The dewar was equipped with quartz windows on both inner and outer walls for incoming exciting light and outgoing luminescence.

Matrix-isolated samples of $[Cr(acac)_3]$ in SF_6 for studies below 77°K were prepared by high-vacuum sublimation from an inductively heated aluminum boat directly onto a cold sapphire window. The matrix-isolation dewar is of conventional design. In the work reported here the sample was prepared at 77°K and then cooled by the introduction of liquid helium to the dewar. Luminescence observations were then made as the sample temperature slowly increased.

A Xe lamp coupled with a monochromator (band pass = 22 nm) was used in obtaining steady-state emission spectra. Exciting light for time-resolved experiments was provided by one of three pulsed laser systems. An AVCO nitrogen laser generated 337.1-nm radiation in pulses of ~5-nsec duration. This wavelength was found to be particularly convenient for the excitation of ligand-localized singlet states in several β-diketonate complexes. One tunable dye laser, utilizing the nitrogen laser as pumping source, consisted of a 1-cm dye cell, Littrow-configuration grating, and an output mirror and could be tuned to any wavelength in the range 350–620 nm. A second tunable dye laser with coaxial flash lamp excitation was used with Rhodamine 6G (R6G) dye to excite the metal-localized $^4T_{2g}$ state of several complexes.

Both steady-state and time-resolved work utilized an RCA C31034A photomultiplier tube in a cooled housing to detect luminescence from the samples. This tube has unusually flat response from 400 nm to beyond 860 nm. In obtaining steady-state emission spectra, a $^3/_4$-m monochromator scanned the wavelength region of interest. In time-resolved experiments, a $^1/_4$-m monochromator and appropriate Corning glass (C) or dielectric (DF) filters provided the wavelength discrimination. The observation direction was at 90° angle to the exciting light.

Steady-state spectra were recorded with the aid of a conventional electrometer and recorder. In time-resolved experiments, the output of the photomultiplier tube after each laser pulse could be displayed on an oscilloscope and the decay curve photographed for later analysis by hand. Matrix-isolated $[Cr(acac)_3]$ decay times were obtained in this way. All other data reported here, however, were obtained by digitization and storage of the output signal in a Biomation 610 transient recorder, signal-averaging over 128 laser pulses in a PDP8/e minicomputer, and subsequent analysis on a larger computer.[6]

III. Results and Discussion

A. Chromium(III) Acetylacetonate. We have studied the time evolution of the ^2E_g state of the complex $[Cr(acac)_3]$

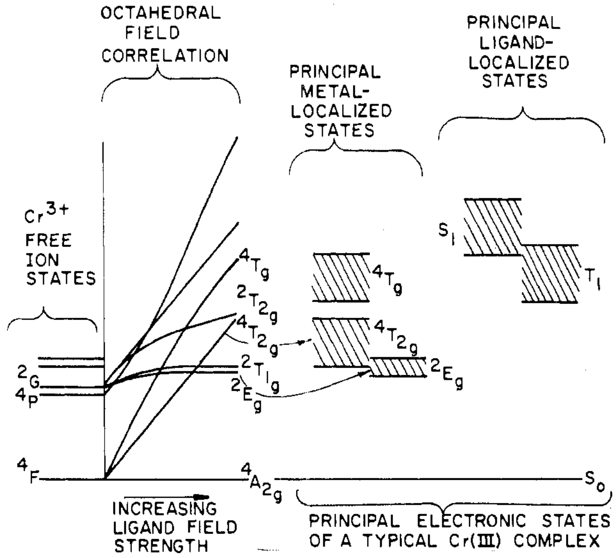

Figure 1. Derivation of the important electronic states of a typical Cr(III) complex.

under a variety of experimental conditions. This complex may be considered the "parent compound" of the whole series of stable Cr(III) β-diketonates, the photophysics of which have been investigated extensively.[3c,7–9] Phosphorescence ($^2E_g \rightarrow {}^4A_{2g}$) was observed at 785 nm (12,700 cm^{-1}). We have found that it is convenient to populate the ^2E_g state via either the metal-localized $^4T_{2g}$ state or the ligand-localized S_1 state. [$Cr(acac)_3$] emission was observed at 77°K in glassy solution and at temperatures from 18 to 77°K in matrix isolation. In methanol–ethanol glasses the lifetime dependence on concentration and laser intensity was investigated.

1. Glass Studies. The [$^4T_{2g} \leftarrow {}^4A_{2g}$] absorption band displays a maximum at about 557 nm (18,000 cm^{-1}) but the band is very broad and is conveniently excited by Rhodamine 6G (R6G) laser emission at 590 nm (17,000 cm^{-1}). The strongly allowed [$S_1 \leftarrow {}^4A_{2g}$] absorption band occurs in the near-ultraviolet region and was conveniently excited by the nitrogen laser at 337.1 nm. The observed ^2E_g lifetime was the same for both modes of excitation. The decay lifetime of [$^2E_g \rightarrow {}^4A_{2g}$] phosphorescence was found to be 437 ± 8 μsec, in good agreement with previous reports.[4a,4b,9] Varying the excitation intensity over three orders of magnitude did not change the lifetime observed. Varying the concentration of the complex in solution from 0.001 *M* to the limit of solubility also had no effect on the lifetime.

In all these experiments, only single exponential decay could be observed. A rise time $\tau_r = 0.1$ μsec should have been clearly evident at any concentration or laser intensity employed here; exponential phenomena as short as 20 nsec should have been observable with high concentrations and 5-nsec laser pulses. Thus the lifetime of the $^4T_{2g}$ state seems to be less than 20 nsec at 77°K and the competition between internal conversion (ic) and intersystem crossing (isc) is such that $k_{ic} + k_{isc} > 5 \times 10^7$ sec^{-1}. The radiative lifetime, $1/k_r$, has been estimated at 2 msec.[10,12] The quantity $k_{isc}k_r/(k_{ic} + k_{isc})$ has been found from the radiative quantum yield upon $^4T_{2g}$ excitation to be approximately 0.14 sec^{-1}.[8] Therefore, we can now *estimate* that the [$^4T_{2g} \rightsquigarrow {}^2E_g$] intersystem crossing rate is $k_{isc} > 10^5$ sec^{-1}.

2. Matrix Isolation Studies. We have pursued the rate of [$^4T_{2g} \rightsquigarrow {}^2E_g$] intersystem crossing at temperatures below 77°K by switching from solvent glass to matrix-isolated environments. The sample was excited by the nitrogen laser at 337.1 nm into the S_1 band of the ligand. The ^2E_g lifetime was found to be temperature independent between 18 and 77°K. ^2E_g phosphorescence was centered at 785 nm (12,300 cm^{-1}) and was observed with 22-nm bandwidth detection. There was evidence of an additional short-lived luminescence at 865 nm (11,600 cm^{-1}) but the source could not be established. Its lifetime at 22°K is about 10 μsec. The observed lifetime of 410 ± 10 μsec is not dramatically different from the 437-μsec lifetime of [$Cr(acac)_3$]/ME, indicating that on the low-temperature "limiting lifetime" plateau, where temperature-dependent processes are not important, the nature of the solvent is also not very important. The luminescence reached its maximum intensity within the resolution time of the experiment, about 1 μsec, indicating that the $^4T_{2g}$ state is apparently depopulated at a rate greater than 10^6 sec^{-1} even at the lowest temperature reached.

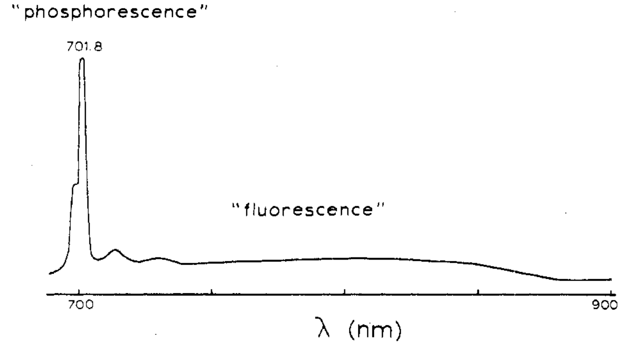

Figure 2. Luminescence spectrum of (saturated) $[Cr(ur)_6]^{3+}$–ME at 77°K; 570–590-nm excitation; 1-nm detection resolution.

B. Hexacyanochromium(III). An understanding of the photophysics of $^4T_{2g}$ and ^2E_g states of $[Cr(CN)_6]^{3-}$ is particularly critical to the photochemistry of this complex since it has recently been shown from sensitization studies that photoaquation apparently occurs from $^4T_{2g}$ state and not the ^2E_g state.[10]

For time-resolved work, the sample was excited by a nitrogen-laser-pumped 2,5-dibiphenyl-1,3,4-oxadiazole (BBD) dye laser tuned to the 377-nm region with 5-nm bandwidth. At 77°K, we observed an excitation spectrum maximum near 377 nm (26,500 cm^{-1}) and an emission spectrum maximum near 805 nm (12,400 cm^{-1}), both values being in good agreement with previous work.[7] The resulting emission displayed a single exponential decay lifetime $\tau = 4.2 \pm 0.2$ msec at 805 nm. The spectral region of this emission was scanned carefully at the best time resolution of the experiment, about 50 nsec, but no luminescence of shorter lifetime could be detected nor could the rise time of the long-lived emission be resolved. Further, the time behavior did not change within an excitation spectral range of approximately 370–385 nm (27,000–26,000 cm^{-1}). Thus our observations confirm those of Castelli and Forster[4b] concerning the rate of appearance of excitation in the ^2E_g state.

C. Chromium(III)–Urea and Chromium(III)–Antipyrene Complexes. $[Cr(ur)_6]^{3+}$ and $[Cr(antip)_6]^{3+}$ are two of perhaps six Cr(III) complexes which are believed to luminescence from two different electronic states.[3a,3b,11] In steady-state emission spectra a narrow band appears near the blue end of a very much broader, structureless band that extends into the infrared region. The former has been assigned to [$^2E_g \rightarrow {}^4A_{2g}$] "phosphorescence". The latter has been assigned to [$^4T_{2g} \rightarrow {}^4A_{2g}$] "fluorescence". (See Figures 2 and 3.) These complexes would appear to offer an excellent opportunity to study directly the nonradiative transition ($^4T_{2g} \leftrightsquigarrow {}^2E_g$) by monitoring emission from both the initial and the terminal states.

1. Spectroscopy. Widely quoted absorption and emission spectra of $[Cr(ur)_6](ClO_4)_3$ have been reported by Porter and Schläfer.[12] Our measured emission spectrum of $[Cr(ur)_6]^{3+}$–ME at 77°K is shown in Figure 4.[3a,b] The broad "fluorescence" feature is notably less intense than in the spectra

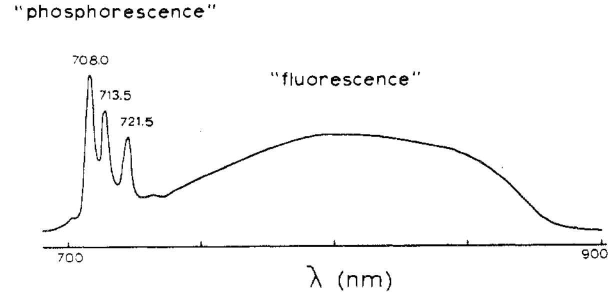

Figure 3. Luminescence spectrum of 0.01 *M* $[Cr(antip)_6]^{3+}$-ME at 77°K; 435–455-nm excitation; 0.5-nm detection resolution.

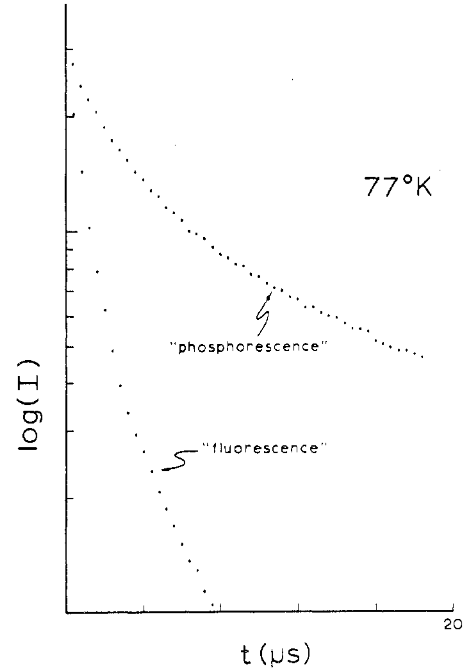

Figure 4. Time behavior of (saturated) $[Cr(ur)_6]^{3+}$-ME luminescence at 77°K; nitrogen-laser-pumped R6G laser excitation at 590 nm. "Phosphorescence" observed at 702 nm; "fluorescence" at 798 nm; 22-nm detection resolution, Corning 2-64 filter.

of some $[Cr(ur)_6]^{3+}$ salts reported by Laver and Smith.[13] The relatively sharp peak at 701.8 nm (14,249 cm^{-1}) has been attributed to "phosphorescence" and its fwhm bandwidth is 3 nm at 0.5-nm resolution. The shoulder on the blue side is real and could not be resolved with 0.5-nm resolution.

The $[Cr(antip)_6]^{3+}$–ME emission spectrum at 77°K, in Figure 3, is similar to that of $[Cr(ur)_6]^{3+}$–ME. The main "phosphorescence" peak appears at 708.0 nm (14,124 cm^{-1}) and the relative amounts of emission were shifted in favor of more "fluorescence". The peaks at 713.5 nm (14,015 cm^{-1}) and 721.5 nm (13,860 cm^{-1}) were quite strong in 0.01 *M* solution but were suppressed at lower concentration (see section C3). Because the steady-state spectrum appeared more interesting, most of the work reported here was done with the $[Cr(antip)_6]^{3+}$ complex.

Dingle[14] has identified the (0, 0) line of the $[{}^4T_{2g} \leftarrow {}^4A_{2g}]$ transition in the $[Cr(ur)_6](NO_3)_3$ crystal absorption spectrum and would place the ${}^4T_{2g}$ state 26.5 ± 4.0 cm^{-1} above the ${}^2E_g$ state. We have been unable to establish definitively the energy ordering of the first excited quartet and doublet states of either complex.

2. Time-Resolved Behavior. We have investigated the time-resolved behavior of luminescence from both $[Cr(ur)_6]^{3+}$–ME and $[Cr(antip)_6]^{3+}$–ME at 77°K after pulsed laser excitation into the ${}^4T_{2g}$ and ${}^4T_{1g}$ absorption bands. The "fluorescence" and "phosphorescence" regions of the spectra for both complexes displayed nonexponential decays.

The ${}^4T_{2g}$ state was excited by the flash-lamp-pumped R6G dye laser at 590 nm (16,900 cm^{-1}) and a nitrogen-laser-pumped R6G dye laser at the same wavelength. The ${}^4T_{1g}$ state of $[Cr(ur)_6]^{3+}$ was excited by a nitrogen-laser-pumped 7-diethylamino-4-methylcoumarin dye laser at 449 nm (22,200 cm^{-1}). The time behavior on ${}^4T_{1g}$ excitation of both "fluorescence" and "phosphorescence" appeared to be the same as on ${}^4T_{2g}$ excitation and the remainder of the experiments employed the latter mode of excitation.

The time-resolved luminescence from $[Cr(ur)_6]^{3+}$ is shown in Figure 4 while that of $[Cr(antip)_6]^{3+}$ at three concentrations in the range 0.01–0.0001 *M* is shown in Figure 5. "Fluorescence" and "phosphorescence" appeared to differ in time dependence. It should be noted that the time behavior of "phosphorescence", and probably "fluorescence", too, is a strong function of concentration. The nonexponentiality is very

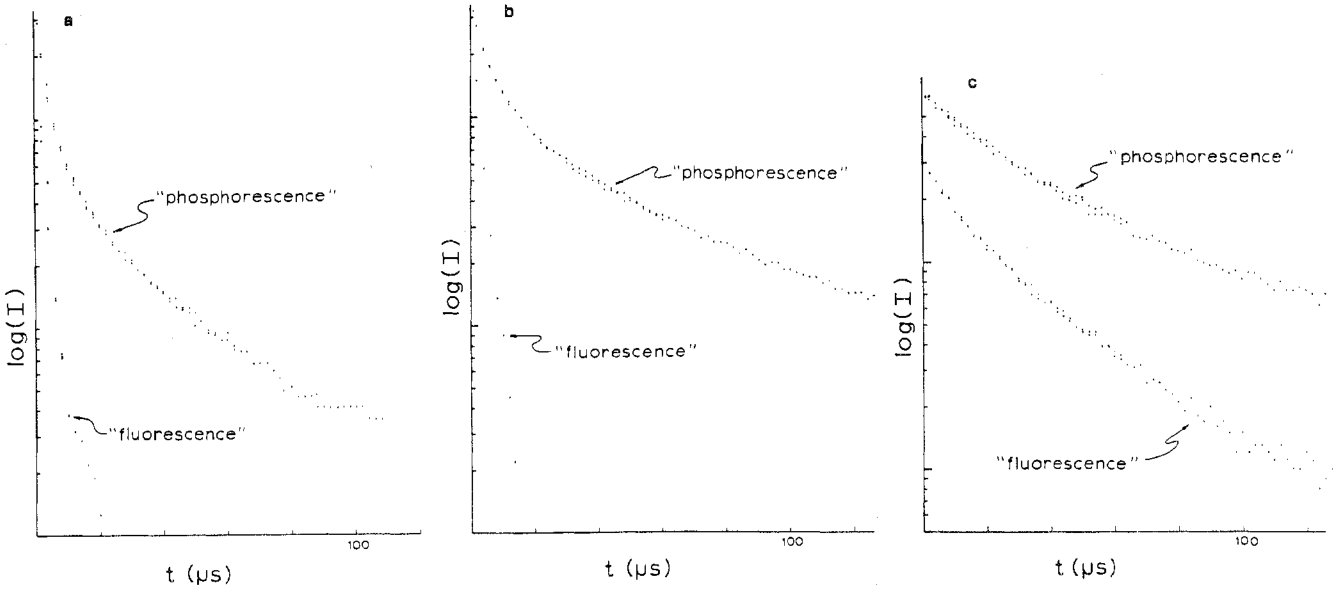

Figure 5. Behavior of $[Cr(antip)_6]^{3+}$-ME luminescence at 77°K. Flash-lamp-pumped R6G laser excitation is at 590 nm. "Phosphorescence" is observed at 709 nm; "fluorescence" at 805 nm; 10-nm detection resolution, Corning 2-58 filter. Data points are from experiments of different time bases: (a) 0.01 *M*; (b) 0.001 *M*; (c) 0.0001 *M*.

Table I. Concentration Dependence of Some Relative Luminescence Quantum Yields of $[Cr(antip)_6]^{3+}$–ME at 77°K

			Phosphorescence structure[c]				
C, *M*	Φ_t[a]	Φ_{fl}/Φ_{ph}[b]	Φ_{701}	Φ_{708}	$\Phi_{713.5}$	$\Phi_{721.5}$	Φ_{731}
10^{-2}	0.10	6.0, 5.9	8.6	100	76	53	6.7
10^{-3}	0.37	5.3, 4.5	2.9	57	33	5.2	
10^{-4}	1.00	4.7	1.4	22	7.6	0.7	

[a] Scaled to $\Phi_t(10^{-4}) = 1.0$, $^4T_{1g}$ excitation. [b] $^4T_{1g}$ excitation, $^4T_{2g}$ excitation. [c] Scaled to $\Phi_{708}(10^{-2}) = 100$, $^4T_{1g}$ excitation.

strong at 0.01 *M*, is less strong at 0.001 *M*, and is small enough at 0.0001 *M* to require a long-time-scale experiment to make it clearly evident. Significantly, at the lowest concentration (0.0001 *M*) and the longest times (100–200 μsec), the data still show curvature on a log (intensity) vs. time plot (see Figure 5c).

The luminescence time behavior observed here is quite different from that reported by Dingle from $[Cr(ur)_6](NO_3)_3$ crystals.[14] In particular, although we did not observe behavior which is immediately interpretable as a sum of exponentials, the long-time-scale slope of a log (intensity) vs. time plot of the "phosphorescence" at 77°K was much longer than Dingle's limit of 10 μsec.

3. Relative Quantum Yields. We have examined the concentration dependence of both the total luminescence quantum yield, Φ_t, and the relative fluorescence-to-phosphorescence quantum yield, Φ_{fl}/Φ_{ph}, for the $[Cr(antip)_6]^{3+}$ complex at 77°K.

Experimentally, steady-state spectra of several $[Cr(antip)_6](NO_3)_3$–ME samples were taken under reproducible conditions so that not only could portions of a spectrum be compared but also the spectra could be compared with each other on a reasonably sound basis. The ability to reproduce a given sample spectrum was shown to be within ±10% by actual experiment on separate days. The functions calculated here were shown to be consistent within 10% for excitation into either the $^4T_{2g}$ or $^4T_{1g}$ bands. The observed difference in optical density between these two methods of excitation was approximately 2. The data are collected in Table I.

The most dramatic concentration effect was the change in the relative total emission quantum yield, Φ_t. On the basis of the light emitted from a 0.001 *M* solution, the emission from a 0.01 *M* solution was only *one-tenth* of that expected from unimolecular decay processes (see Table I). The change in Φ_t with concentration represented principally an overall reduction in "intensity" since the relative amounts of "phosphorescence" and "fluorescence", Φ_{fl}/Φ_{ph}, did not change substantially.

Part of the "phosphorescence" structure, shown in Figure 6, was strongly affected by the concentration of the complex. The peaks at 713.5 and 721.5 nm clearly diminished with respect to the principal line at 701.8 nm on dilution. The relative intensities of these peaks have been approximated in Table I.

4. Energy Transfer. Recently, Laver and Smith[13] showed that the "fluorescence" quantum yields of several $[Cr(ur)_6]^{3+}$ salts displayed a maximum as the temperature was lowered. The simplest interpretation of this evidence was that, although the $^4T_{2g}$ state is populated directly by absorption, $[^4T_{2g} \leftrightarrow {}^2E_g]$ intersystem crossing is rapid and the $^4T_{2g}$ state is continually repopulated by a ^2E_g state of similar energy. Under this interpretation, nearly all of the $[^4T_{2g} \rightarrow {}^4A_{2g}]$ "fluorescence" intensity is "delayed thermal fluorescence".

The experiments on $[Cr(ur)_6]^{3+}$ and $[Cr(antip)_6]^{3+}$ in this work add several new aspects to the photophysical processes of these complexes. The decay behavior was certainly not a single exponential nor did it appear to be a simple double exponential. Double-exponential decay of both "fluorescence" and "phosphorescence" would have been expected for any model in which the $^4T_{2g}$ state comes into equilibrium with the ^2E_g state through first-order kinetics; "delayed thermal fluorescence" is a special case of this model.

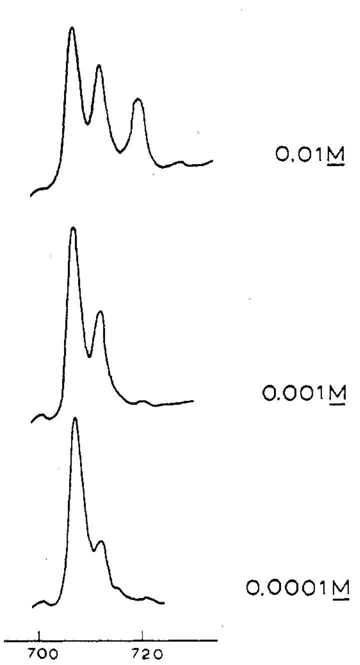

Figure 6. Concentration dependence of the luminescence spectrum of $[Cr(antip)_6]^{3+}$–ME at 77°K. All three spectra were taken under the same condition as Figure 5. Note the loss of "phosphorescence" structure on dilution (see text).

The relative total quantum yield, Φ_t, decreased with increasing concentration, indicating that as the molecules of the complex became more densely packed, electronic energy found itself more accessible to nonradiative quenching. Such quenching could occur either in traps that are present at all concentrations or in traps created on increasing the concentration of the complex. One simple interpretation of the increasing prominence of two "phosphorescence" shoulder peaks relative to the principal peak is that they are emission from associated molecules, i.e., dimerized complexes, trimerized complexes, etc. These oligomers must decay nonradiatively at a faster rate than the monomers in order to account for the observed trend in Φ_t.

The complete picture of the photophysics of the $^4T_{2g}$ and ^2E_g states of these complexes undoubtedly deserves further interest. In light of the results reported here, we would add the precautionary note that, until that picture is complete, $[Cr(ur)_6]^{3+}$ and $[Cr(antip)_6]^{3+}$ ought to be used as examples of "delayed thermal fluorescence" only with due caution.

IV. Conclusions

The application of pulsed laser excitation to luminescence studies of chromium(III) complexes has expanded the time resolution of our photophysical interest in coordination compounds to the nanosecond range. In time-resolved, wavelength-resolved investigations of three "phosphorescent" complexes, $[Cr(acac)_3]$, $[Cr(CN)_6]^{3-}$, and $[Cr(dbm)_3]$, $^4T_{2g}$ fluorescence was not observed and the rise time of ^2E_g phosphorescence via intersystem crossing was faster than the time resolution of these experiments. The lifetime of the $^4T_{2g}$ state in $[Cr(acac)_3]$ at 77°K can now be estimated at $<10^{-5}$ sec. It would appear that picosecond time resolution may be necessary to observe these processes.

On the other hand, time-resolved, wavelength-resolved studies of $[Cr(ur)_6]^{3+}$ and $[Cr(antip)_6]^{3+}$ affirm that both ^2E_g phosphorescence and $^4T_{2g}$ fluorescence are observed on excitation of the $^4T_{2g}$ or $^4T_{1g}$ states. However, in our experiments the decays of these emissions are not single exponentials nor can they be adequately described by any three-state equilibrium model, which would yield double-exponential decays. Furthermore, the time behavior of the emissions as well as the quantum efficiencies for luminescence and certain features of the emission spectra are all dependent upon the concentration of the complexes in the solvent matrix. These two complexes appear to provide the best opportunities for examining the photophysical interactions between excited electronic states in chromium(III) systems.

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Registry No. [Cr(ur)$_6$]Cl$_3$, 14023-01-9; [Cr(antip)$_6$](NO$_3$)$_3$, 55660-57-6; K$_3$[Cr(CN)$_6$], 13601-11-1; [Cr(acac)$_3$], 13681-82-8.

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Contribution from the Departments of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic Properties and Bonding of the Pyrido[2,3-*b*]pyrazine and the 1,5-Naphthyridine Complexes of Copper(II) Nitrate

HENRY J. STOKLOSA,[1a] JOHN R. WASSON,*[1a] ELLIS V. BROWN,[1a] H. WAYNE RICHARDSON,[1b] and WILLIAM E. HATFIELD[1b]

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The 1:1 pyrido[2,3-*b*]pyrazine adduct of copper(II) nitrate has been prepared and characterized using magnetic susceptibility measurements and electronic and infrared spectroscopy. Semiempirical molecular orbital calculations have been employed to characterize ligands of the pyrazine type as well as the pyrazine adduct of copper(II) nitrate. The latter calculations provide a basis for the interpretation of the properties of several heterocyclic amine adducts of copper(II) nitrate. The 1,5-naphthyridine complex of copper(II) nitrate has also been prepared, and the structure which was deduced from low-temperature magnetic susceptibility and spectroscopic studies supports the novel structure assigned to the pyrido-[2,3-*b*]pyrazine complex.

Introduction

A number of polymeric complexes of the general type CuLX$_2$ (L = heterocyclic amine, X = halide, NO$_3^-$) have been prepared and characterized.[2–9] In an effort to assess the change in bonding by a different arrangement of nitrogen atoms in the heterocyclic amine ligand the pyrido[2,3-*b*]pyrazine adduct of copper(II) nitrate has been prepared and compared with the pyrazine,[7,8] quinoxaline,[9] and 1,5-naphthyridine adducts of copper(II) nitrate. The results of the present study indicate that the nitrate ions are bidentate ligands as found in the structure[6] of the 1:1 pyrazine–copper(II) nitrate complex and the proposed structure of the pyrido[2,3-*b*]pyrazine (PP) complex is given in Figure 1. Earlier studies of copper(II) complexes of this type have indicated the presence of antiferromagnetic exchange interactions.[5] Billing et al.[5] postulated that exchange coupling between copper(II) ions occurred via the bidentate heterocyclic ligand even though the room-temperature magnetic moment was normal. Such an exchange interaction was found[7,8] for the 1:1 pyrazine–copper(II) nitrate compound and is probably present in the polymeric adducts of copper(II) halides with pyridazine, phthalazine, and 3,4-benzocinnoline.[10]

In the present work the magnetic susceptibility of (PP)Cu(NO$_3$)$_2$ and (nap)Cu(NO$_3$)$_2$ is reported. The infrared and electronic spectrum of (PP)Cu(NO$_3$)$_2$ is also included. The results of simple Hückel molecular orbital calculations for the ligands and extended Hückel MO calculations for pyrazinecopper(II) nitrate have been utilized to elucidate the electronic structure of polymeric complexes of the type [CuL(NO$_3$)$_2$]$_n$ where L is a bridging heterocyclic amine.

Experimental Section

Pyrido[2,3-*b*]pyrazine was obtained from Aldrich Chemical Co., Milwaukee, Wis., and used as received. The 1,5-naphthyridine was prepared by the method of Hamada and Takeuchi.[11] All other chemicals were of the best available reagent grades. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Preparation of Pyrido[2,3-*b*]pyrazinecopper(II) Nitrate, (PP)Cu(NO$_3$)$_2$, and (1,5-Naphthyridine)copper(II) Nitrate, (nap)Cu(NO$_3$)$_2$. The complexes were obtained by adding a 1 *M* solution of copper(II) nitrate trihydrate in methanol (which also contained sufficient 2,2-dimethoxypropane for removal of water) dropwise with vigorous stirring to a 1 *M* solution of the ligand in methanol. The blue complex which precipitated was isolated by filtration, washed with several small portions of methanol followed by ether, and then air-dried.

Anal. Calcd for Cu(C$_7$H$_5$N$_3$)(NO$_3$)$_2$: C, 26.38; H, 1.58; N, 21.09.