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Photochemical and Photophysical Behavior of *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III)

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Abstract: The photochemistry and luminescence of *trans*-$Cr(en)_2(NCS)_2^+$ have been investigated in acidic aqueous solutions under direct irradiation, sensitization, and quenching conditions. Irradiation in the ligand field bands causes two photoreactions, NCS^- release and H^+ consumption, the latter reaction being due to the protonation of a detached ethylenediamine end. Within the experimental errors, Φ_{H^+} is constant (0.07) for both charge transfer and ligand field excitation, whereas Φ_{NCS^-} is constant (0.18) in the LF region but decreases (0.13) on CT excitation. CT excitation also causes a redox decomposition of the complex, which has been evidenced by scavenging Cr(II) species with $Co(NH_3)_5Cl^{2+}$. The relative phosphorescence quantum yield is constant from 330 to 540 nm (ligand field region), but it decreases both in the CT region and in the low-energy tail of the lowest quartet LF band. Sensitization by $Ru(bpy)_2(CN)_2$ causes both photosubstitution reactions with limiting quantum yields which are equal to the quantum yields obtained upon direct irradiation in the LF bands. In contrast, the limiting quantum yield of the sensitized emission is 25% higher than the quantum yield of phosphorescence upon direct LF irradiation. Quenching by $Cr(CN)_6^{3-}$ causes a parallel quenching of the phosphorescence emission and lifetime of *trans*-$Cr(en)_2$-$(NCS)_2^+$. Complete phosphorescence quenching leaves 20% of unquenchable part for both NCS^- release and en detachment. The results indicate that both photoreactions originate from the same excited state which, in a traditional Jablonsky diagram, is the lowest quartet excited state, $^4T_{2g}$. The results are also discussed on the basis of the spin–orbit coupling framework recently proposed by Kane-Maguire et al.

Introduction

Cr(III) complexes have played a fundamental role in the early development of inorganic photochemistry.[1-3] In the last few years, the discovery[4,5] that several Cr(III) complexes exhibit appreciable phosphorescence under experimental conditions in which photochemistry can also be observed has stimulated the use of quenching[5-14] and sensitization[15-17] techniques[18] with the aim of elucidating the excited state mechanism of these photoreactions. In addition, the study of mixed-ligand complexes has been extended[19-31] and important results have been obtained concerning the preferential ligand labilization and the stereochemistry of the photosubstitution reactions. Numerous theoretical papers[32-37] have also appeared with the aim of rationalizing and predicting the photochemistry of Cr(III) complexes on the basis of current MO models. Other recent important results on Cr(III) photochemistry are those concerning the redox decomposition of acido pentaammine complexes,[38] the bimolecular redox reactions of the lowest excited state of $Cr(bpy)_3^{3+}$,[39,40] the measurement of the $^4T_2 \leadsto {}^2E$ intersystem crossing efficiency,[41] and the finding that its value may depend on the excitation wavelength.[13,42] The accumulation of these results reveals new subtle aspects of Cr(III) photochemistry and calls for more informative experiments. For example, it would be very interesting to extend the comparison between phosphorescence and photochemistry under quenching or sensitization conditions to complexes which undergo *two* distinct photoreactions. *trans*-$Cr(en)_2(NCS)_2^+$ is suitable for such experiments since

it is able to exhibit both a relatively strong phosphorescence in aqueous solution at room temperature[4] and two distinct, sufficiently efficient photoreactions.[25] This complex is also interesting because it shows intense charge transfer bands in the near UV region and is therefore suitable for a comparative study of charge transfer and ligand field photochemistry.

In this paper we report the results of a systematic investigation on the photochemistry and phosphorescence of trans-$Cr(en)_2(NCS)_2^{2+}$ in aqueous solution upon direct excitation at several different wavelengths, sensitization by Ru-$(bpy)_2(CN)_2$, and quenching by $Cr(CN)_6^{3-}$.[43]

Experimental Section

Materials. *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III)thiocyanate, *trans*-$[Cr(en)_2(NCS)_2]NCS$, was prepared from $[Cr(en)_3](NCS)_3$ according to the method of Rollinson and Bailar.[45] The compound so obtained was recrystallized from water, transformed into the perchlorate salt, *trans*-$[Cr(en)_2(NCS)_2]ClO_4$, and then recrystallized three times from water. The spectral characteristics of the complex were in fair agreement with those given by Bifano and Linck.[25] Pure samples of $[Ru(bpy)_3]Cl_2$ (bpy = 2,2'-bipyridine),[14] $Ru(bpy)_2(CN)_2$,[14] $K_3[Cr(CN)_6]$,[16] $[Co(NH_3)_5Cl]Cl_2$,[1] and $[Cr(bpy)_3](ClO_4)_3$[41] were available from previous investigations. All the other chemicals were of reagent grade.

Apparatus. For the photochemical experiments, radiations of 313, 365, 437, and 508 nm were obtained as previously described,[46] whereas 530- and 560-nm radiations were obtained from the Perkin-Elmer MPF 3 spectrofluorimeter with 20-nm band-pass width. The intensity of the incident light, which was measured by means of the ferric oxalate[47] or reineckate[48] actinometers, was of the order of 10^{-7} $N h\nu$/min

for 313, 365, 437, 508, and 530 nm. Owing to experimental difficulties, for 560 nm only the relative light intensity was measured with the method described under Procedures. The fraction of absorbed light was calculated from the optical density of the irradiated solutions. The reaction cells were standard spectrophotometric cells (thickness, 1 cm; capacity, 3 mL) housed in a thermostated cell holder. The absorbance measurements and the recording of the spectra were performed with a Shimadzu QV-50 and a Perkin-Elmer 323 spectrophotometer. pH measurements were made by a Knick KpH 34 pH meter equipped with an Ingold Lot-type combined microelectrode. Emission spectra were recorded with a Hitachi Perkin-Elmer MPF 3 spectrofluorimeter. Emission lifetimes were measured with an apparatus based on a pulsed nitrogen laser, and equipped with a R-446 tube and a Tektronix transient digitizer.[49]

Procedures. Unless otherwise noted, the experiments were carried out in air-equilibrated aqueous solution, pH 3 (HClO$_4$), 15 °C. When necessary, deaeration was carried out by bubbling a stream of purified nitrogen for 30 min. The complex concentration was generally 1 × 10^{-2} M.

For the photolysis experiments the general procedure was as follows. The reaction cell was filled with 3 mL of the solution and placed in the thermostated cell holder of the irradiation equipment. A sample of the same solution was maintained in the dark at the same temperature in order to provide a control for thermal reactions. The irradiated solution was stirred with a stream of air or nitrogen. In each experiment, no more than 10% of the reactant was decomposed in order to avoid secondary photochemical reactions. The pH variations were continuously monitored during irradiation. The pH changes were converted into changes of the H$^+$ concentration by means of a ΔpH vs. Δ[H$^+$] calibration plot obtained by adding known amounts of base to a portion of the same solution maintained in the dark. The amount of NCS$^-$ released was measured after suitable irradiation periods by means of the iron thiocyanate method.[48] The concentration of Co^{2+} formed in the experiments carried out in the presence of [Co(NH$_3$)$_5$Cl]Cl$_2$ was measured by the method of Vydra and Pribil.[50] In each case, a sample of the corresponding dark solution was analyzed in the same way. In the photosensitization experiments, 93% of the exciting light (437 nm) was absorbed by the Ru(bpy)$_2$(CN)$_2$ sensitizer (3 × 10^{-4} M) and appropriate corrections were performed in order to obtain the sensitization quantum yield. In the quenching experiments, the maximum concentration of the quencher was 10^{-2} M. The thermal aquation of Cr(CN)$_6^{3-}$ during the experiments was always less than 5%. The exciting light (508 nm) was only absorbed by *trans*-Cr(en)$_2$(NCS)$_2^+$.

The relative quantum yield of phosphorescence emission at different excitation wavelengths was measured by a method based on the use of Ru(bpy)$_3^{2+}$ as a quantum counter. This complex is known to exhibit a wavelength-independent phosphorescence quantum yield.[51] The phosphorescence intensity (at 728 nm) of the Cr complex upon excitation at λ_{ex}^1 is given by

$$I_p(\lambda_{ex}^1) = \alpha I_A(\lambda_{ex}^1)\Phi_p(\lambda_{ex}^1) \qquad (1)$$

where α is a proportionality constant and $I_A(\lambda_{ex}^1)$ and $\Phi_p(\lambda_{ex}^1)$ are the absorbed intensity and the quantum yield of phosphorescence emission upon excitation at λ_{ex}^1. If emission intensity measurements are carried out at two different excitation wavelengths with the same emission slit, the proportionality constant is the same and the ratio between the quantum yields of phosphorescence at the two different excitation wavelengths is given by

$$\frac{\Phi_p(\lambda_{ex}^1)}{\Phi_p(\lambda_{ex}^2)} = \frac{I_p(\lambda_{ex}^1)}{I_p(\lambda_{ex}^2)}\frac{I_A(\lambda_{ex}^2)}{I_A(\lambda_{ex}^1)} \qquad (2)$$

For solutions having the same optical density at the respective excitation wavelengths, the second term on the right-hand side of eq 2 is equal to the ratio of the respective incident light intensities. This last quantity was obtained by comparing emission signals of absorbance-matched solutions of Ru(bpy)$_3^{2+}$ under identical slit conditions.

For the experiments concerning the quenching of the phosphorescence intensity, the excitation wavelength was 490 nm and the emission was monitored at 728 nm (peak of the emission band). For the emission decay measurements, the excitation wavelength was 337 nm and the emission was monitored at 728 nm. The experiments concerning the sensitization of the phosphorescence emission by Ru(bpy)$_2$(CN)$_2$ were carried out as indicated in ref 41. In all cases

Table I. Photoreaction Quantum Yields[a]

Excitation λ, nm	Φ$_{NCS^-}$[b]	Φ$_{H^+}$[c]	Remarks
313	0.13	0.07	
313[d]			[Co(NH$_3$)$_5$Cl^{2+}] = 5 × 10^{-3}, Φ$_{Co_{aq}^{2+}}$ = 7 × 10^{-4}
313[d]			[Co(NH$_3$)$_5$Cl^{2+}] = 1.5 × 10^{-2}, Φ$_{Co_{aq}^{2+}}$ = 4 × 10^{-3}
365	0.18	0.07	
437[e]	0.19	0.07	[Ru(bpy)$_2$(CN)$_2$] = 3 × 10^{-4}
508	0.18	0.07	
508[f]	0.11		[Cr(CN)$_6^{3-}$] = 7 × 10^{-5}
508[f]	0.07		[Cr(CN)$_6^{3-}$] = 1.5 × 10^{-4}
508[f]	0.06		[Cr(CN)$_6^{3-}$] = 3.5 × 10^{-4}
508[f]	0.05	0.016	[Cr(CN)$_6^{3-}$] = 5 × 10^{-4}
508[f]	0.03		[Cr(CN)$_6^{3-}$] = 7 × 10^{-4}
508[f]	0.04		[Cr(CN)$_6^{3-}$] = 1 × 10^{-3}
508[f]	0.03	0.015	[Cr(CN)$_6^{3-}$] = 1 × 10^{-2}
508[d]			[Co(NH$_3$)$_5$Cl^{2+}] = 1 × 10^{-2}, Φ$_{Co_{aq}^{2+}}$ < 1 × 10^{-4}
530	0.18		
560[g]	(0.18)		

[a] 15 °C, pH 3 (HClO$_4$), air-equilibrated solutions. [b] Quantum yield of NCS$^-$ formation. [c] Quantum yield of H$^+$ consumption. [d] Cr(II) scavenger experiments. [e] Sensitization experiments. [f] Quenching experiments; other quenching data are reported in ref 44. [g] The relative quantum yield of NCS$^-$ release was found to be the same at 530 and 560 nm.

the emission intensities were extrapolated to zero time as the solutions were slightly photolyzed by the exciting light.

Results

Photochemical Experiments. The absorption spectrum of *trans*-Cr(en)$_2$(NCS)$_2^+$ is shown in Figure 1. There are ligand (NCS$^-$) to metal charge transfer bands in the UV region[52] and ligand field bands in the visible. At each one of the excitation wavelengths, irradiation caused the release of NCS$^-$ ions and an increase in the pH of the solution. For short irradiation periods the concentrations of NCS$^-$ and H$^+$ changed linearly with the number of absorbed einsteins. No postphotochemical effect was observed. The photochemical behavior was qualitatively the same also in the presence of Ru(bpy)$_2$(CN)$_2$ as a potential sensitizer and of Cr(CN)$_6^{3-}$ as a potential quencher.[43] The quantum yields of H$^+$ consumption and NCS$^-$ release under the various experimental conditions are gathered in Table I. The values reported are the average of three or four independent runs (mean deviation ~10%). Deaeration of the solution did not cause appreciable changes in the quantum yields. Experiments carried out at 530 and 560 nm, using the method reported in the Procedures for the phosphorescence quantum yield, showed that the relative quantum yield of NCS$^-$ release is the same at these wavelengths. The quantum yields of the two direct, unquenched photoreactions as a function of the excitation wavelength are also displayed in Figure 1.

Both Φ$_{NCS^-}$ and Φ$_{H^+}$ were found to decrease in the presence of Cr(CN)$_6^{3-}$. The corresponding Stern–Volmer quenching plots are shown in Figure 2.

When solutions containing *trans*-Cr(en)$_2$(NCS)$_2^+$ (1.5 × 10^{-2} M) and Co(NH$_3$)$_5$Cl^{2+} were irradiated at 313 nm, Co^{2+} was produced. This did not happen upon 508-nm irradiation. The quantum yields of Co^{2+} production (after correction for the Co^{2+} formed upon direct light absorption by Co(NH$_3$)$_5$Cl^{2+}) are also reported in Table I.

Luminescence Experiments. The complex shows a narrow emission band centered at 728 nm, which is due to the $^2E \rightsquigarrow$ $^4A_2$ phosphorescence.[4] The phosphorescence intensity increases slightly (≤5%) upon deaeration of the solution. The first-order rate constant of phosphorescence decay was found to be 9.5 ×

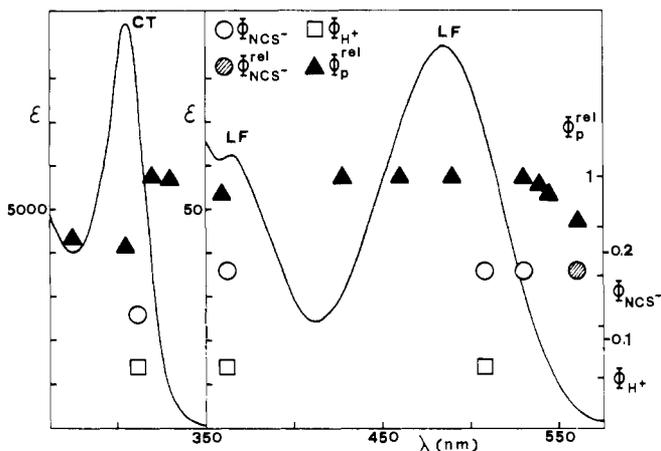**Figure 1.** Absorption spectrum, reaction quantum yields, and relative phosphorescence quantum yield of *trans*-Cr(en)$_2$(NCS)$_2^+$ at various irradiation wavelengths (aqueous solution, pH 3, 15 °C). The relative phosphorescence quantum yield has been taken to be unity at 490 nm.
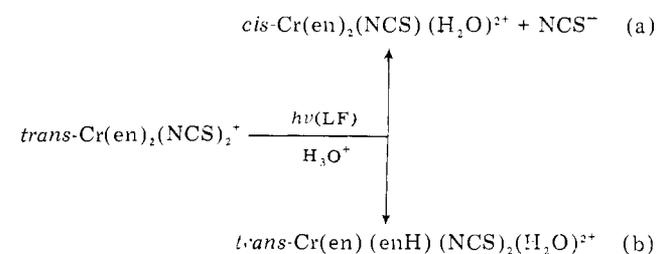

Figure 2. Stern–Volmer quenching plots for the phosphorescence lifetime and the quantum yields of phosphorescence emission, NCS$^-$ release, and H$^+$ consumption.

10^4 s^{-1} (τ = 10.5 μs) in air-equilibrated solutions, pH 3, 15 °C. Phosphorescence intensities of absorbance-matched *trans*-Cr(en)$_2$(NCS)$_2^+$ and Ru(bpy)$_3^{2+}$ solutions were measured as described in the Procedure. The data so obtained were used (eq 2) to determine the relative phosphorescence quantum yield, Φ_p^{rel}, as a function of the excitation wavelength. The results obtained are displayed in Figure 1, where the quantum yield of phosphorescence upon 490-nm excitation has been taken as unity.

The quenching of the phosphorescence intensity was studied with various concentrations of Cr(CN)$_6^{3-}$ as a potential quencher. Lifetime measurements showed that the phosphorescence lifetime was quenched in parallel with the phosphorescence intensity. The Stern–Volmer quenching plots are shown in Figure 2.

As previously shown by Bolletta et al.,[41] Ru(bpy)$_2$(CN)$_2$ was found to sensitize the phosphorescence of *trans*-Cr-(en)$_2$(NCS)$_2^+$. The ratio between the quantum yield of direct and (limiting) sensitized phosphorescence was found to be ~0.8, a value noticeably higher than that found previously.[41] A reinvestigation of the donor–acceptor couples dealt with in ref 41 is now in course with the aim of understanding the reason for the discrepancy. The results obtained so far[53] seem to indicate that the previously reported value was wrong.

Discussion

The photolysis of *trans*-Cr(en)$_2$(NCS)$_2^+$ in dilute acid media was studied by Bifano and Linck[25] using four irradiation wavelengths in the 400–520-nm range (ligand field bands). They identified two reaction products, *cis*-Cr(en)$_2$(NCS)-(H$_2$O)$^{2+}$ and a molecule of stoichiometry Cr(en)(enH)-(NCS)$_2$(H$_2$O)$^{2+}$ that was assigned a structure with thiocyanate groups trans to each other:

$$cis\text{-}Cr(en)_2(NCS)(H_2O)^{2+} + NCS^- \quad (a)$$

$$trans\text{-}Cr(en)_2(NCS)_2^+ \xrightarrow[\text{H}_3\text{O}^+]{h\nu(\text{LF})}$$

$$trans\text{-}Cr(en)(enH)(NCS)_2(H_2O)^{2+} \quad (b)$$

According to the same authors, the quantum yield of photoreaction (a) was 0.24 at 23 °C, independent of the exciting wavelength, and the quantum yield of photoreaction (b) was 0.1, with a scattered wavelength dependence. We have mea-
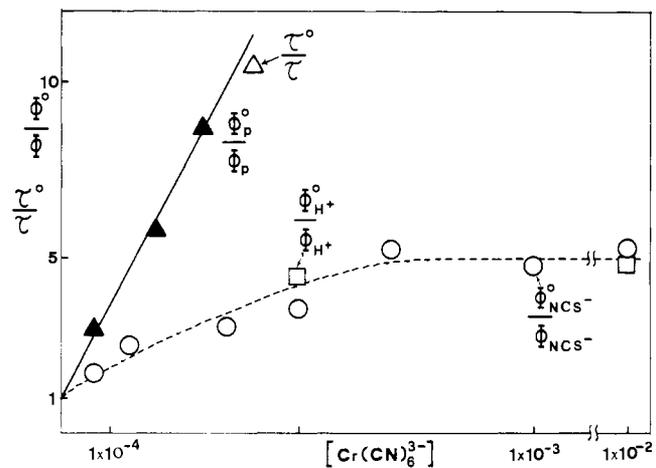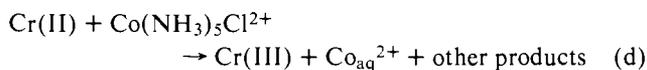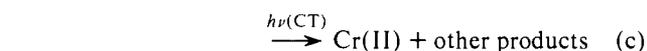
sured the quantum yield of reaction (a) from the NCS$^-$ release and the quantum yield of reaction (b) from the proton uptake. The results obtained (Table I) are in fair agreement with those of Bifano and Linck[25] if one consideres the different temperature (our experiments were carried out at 15 °C) and the experimental errors which are unavoidably large in chromatographic analyses such as those used in ref 25.

Bifano and Linck's[25] interest was centered on the stereochemistry of the two photoreactions and on the role of σ and π bonding in determining the preferential ligand labilization, with the tacit assumption that the photoreactions originate from the lowest quartet excited state ($^4T_{2g}$ in octahedral symmetry). We are mainly interested in the role played by the various excited states in determining the photochemical and photophysical properties. We will first examine the results obtained and then try to draw some conclusion concerning the excited state behavior.

Photoreaction Quantum Yield. The results obtained (Figure 1) show that the quantum yield of reaction (b) is wavelength independent in all the wavelength range examined. The quantum yield of reaction (a) is constant between 365 and 560 nm, but it decreases upon 313-nm excitation (CT band). Irradiation at this wavelength in the presence of Co(NH$_3$)$_5$Cl^{2+} causes the formation of some Co^{2+} (Table I). Since Co(NH$_3$)$_5$Cl^{2+} is an excellent scavenger for Cr(II) (yielding Co^{2+} and Cr(III) species),[54] this result indicates that CT excitation causes a redox decomposition of *trans*-Cr(en)$_2$-(NCS)$_2^+$ (see also ref 38):

$$trans\text{-}Cr(en)_2(NCS)_2^+$$
$$\xrightarrow{h\nu(\text{CT})} Cr(II) + \text{other products} \quad (c)$$

$$Cr(II) + Co(NH_3)_5Cl^{2+}$$
$$\rightarrow Cr(III) + Co_{aq}^{2+} + \text{other products} \quad (d)$$

The quantum yield of Co$_{aq}^{2+}$ formation (Table I) is, of course, a lower limiting value for the quantum yield of reaction (c). An upper limiting value of 0.3 for the quantum yield of the same reaction is placed by the inefficiency of the CT ⤳ LF internal conversion (see below). Irradiation at 508 nm in the presence of Co(NH$_3$)$_5$Cl^{2+} did not cause any appreciable Co$_{aq}^{2+}$ formation, showing that no redox decomposition of *trans*-Cr(en)$_2$(NCS)$_2^+$ occurs upon ligand field irradiation.

The constancy of Φ_{NCS^-} and Φ_{H^+} in the ligand field region indicates that reactions (a) and (b) originate from either the lowest excited quartet or the lower lying doublets (for a more complete discussion, see below). The lower quantum yield of
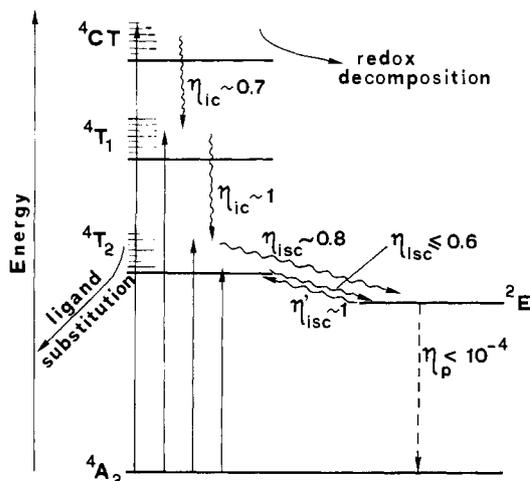
Figure 3. Schematic energy level diagram for *trans*-Cr(en)$_2$(NCS)$_2^+$: ^{4}CT is a spin-allowed charge transfer excited state; ^{4}T$_1$ and ^{4}T$_2$ are the spin-allowed metal-centered excited states; ^{2}E is the lowest spin-forbidden metal-centered excited state. Higher energy doublets are not shown for the sake of simplicity. The efficiencies of various steps are indicated.

Figure 4. Comparison between photolysis and phosphorescence quenching by Cr(CN)$_6^{3-}$

NCS$^-$ release upon CT excitation indicates that reaction (c) (or some other deactivation process) competes with internal conversion from CT to LF excited states. The constancy of Φ_{H^+} in going from LF to CT excitation is presumably due to the fact that the inefficiency of the CT $\leadsto$ LF internal conversion is made up by some contribution of reaction (c) to proton uptake.

Phosphorescence Quantum Yield. The phosphorescence emissions of *trans*-Cr(en)$_2$(NCS)$_2^+$ and Cr(bpy)$_3^{3+}$ occur at the same wavelength.[4] Experiments performed under the same instrumental conditions have shown that the phosphorescence intensity of *trans*-Cr(en)$_2$(NCS)$_2^+$ is approximately seven times lower than that of Cr(bpy)$_3^{3+}$. Since the phosphoresence quantum yield of Cr(bpy)$_3^{3+}$ is lower than 10^{-3},[14] we must conclude that the phosphorescence quantum yield of *trans*-Cr(en)$_2$(NCS)$_2^+$ is $<10^{-4}$.

Figure 1 shows the relative quantum yield of phosphorescence (Φ_p^{rel}) as a function of the irradiation wavelength. As one can see, Φ_p^{rel} increases in going from CT to LF excitation, remains constant in the ligand field region from 330 to 540 nm, and decreases in the tail of the lowest ligand field band. A similar decrease of Φ_p^{rel} in the tail of the lowest ligand field region from 330 to 540 mm, and decreases in the tail of the lowest ligand field band has recently been observed for Cr(en)$_3^{3+}$ and Cr(NH$_3$)$_6^{3+}$ by Kane-Maguire et al.[13,42] The phosphorescence quantum yield is given by the quantum yield of doublet formation, $\varphi(^2E_g)$, times the efficiency of doublet emission, η_p.[55]

$$\varphi_p = \varphi(^2E_g)\eta_p$$

As η_p is an intrinsic property of the emitting state, a change of φ_p with excitation wavelength means that the quantum yield of doublet formation changes with excitation wavelength. Thus, making reference to the simplified (and traditional) energy level diagram of Figure 3, our results (Figure 1) indicate that (1) the efficiency of internal conversion of the CT excited state to ligand field states is $\sim$0.7, and (2) the efficiency of intersystem crossing from the lowest quartet ligand field to the doublet emitting state varies with the amount of vibrational energy available to the quartet. Stated in other words, (1) in the CT excited state there are deactivation paths that compete with internal conversion to the lower lying LF states,[56] and (2) in the lowest quartet ligand field state, intersystem crossing to the doublet competes with vibrational relaxation (see also ref 13 and 42).
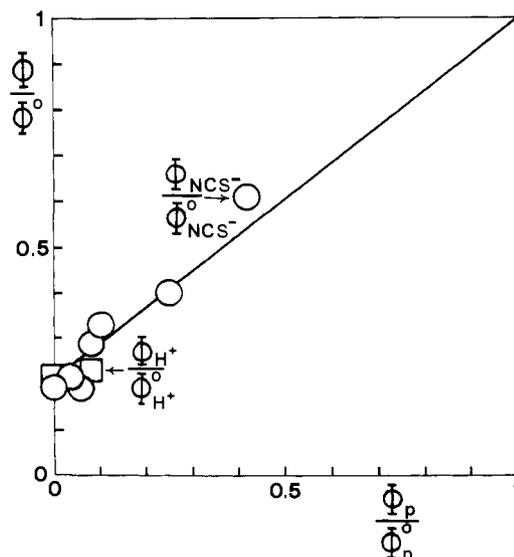
Sensitization Experiments. *trans*-Cr(en)$_2$(NCS)$_2^+$ has the lowest doublet, ^{2}E, at 1.38 μm^{-1} and another doublet, ^{2}T$_1$, at slightly higher energy.[57,58] The zero vibrational level of the lowest excited quartet, ^{4}T$_2$, is estimated to be at 1.83 μm^{-1} above the ground state,[60] but the absorption maximum is at 2.02 μm^{-1} (Figure 1). The donor used, Ru(bpy)$_2$(CN)$_2$, is known to emit from a CT excited state which is formally a triplet. The zero vibrational level of this excited state is estimated to be at 1.85 μm^{-1},[61] in rigid matrix at 77 K, but the emission band in aqueous solution shows its maximum at $\sim$1.6 μm^{-1}. Thus, energy transfer from the donor excited state to give the ^{4}T$_2$ excited state of *trans*-Cr(en)$_2$(NCS)$_2^+$ has to be a "nonvertical", thermally activated process and is therefore expected to be slow.[62] On the contrary, vertical energy transfer to give the ^{2}E (or the upper doublet) excited state of the acceptor is exothermic. On the other hand, energy transfer from triplet donors to both quartet and doublet excited states in Cr(III) complexes is spin allowed.[18] Thus, it seems likely that Ru(bpy)$_2$(CN)$_2$ sensitization only populates the ^{2}E state of the acceptor. We have found that the ratio between the quantum yield of phosphorescence upon direct irradiation (330–530 nm) and the (limiting) quantum yield of phosphorescence upon Ru(bpy)$_2$(CN)$_2$ sensitization is $\sim$0.8. This means that, as the intersystem crossing efficiency of the donor is known to be $\sim$1,[41,63] the ^{4}T$_2$ $\leadsto$ ^{2}E intersystem crossing efficiency from high vibrational levels of ^{4}T$_2$ is $\sim$0.8. On the other hand, as the relative phosphorescence quantum yield decreases by more than 20% in the tail of the ^{4}T$_2$ band (Figure 1), the intersystem crossing efficiency from the thermally equilibrated ^{4}T$_2$ state to ^{2}E has to be $\leq$0.6 (Figure 3).

It is also very important to note that for both photoreactions (a) and (b) sensitization by Ru(bpy)$_2$(CN)$_2$ yields the same (limiting) quantum yield as direct excitation in the LF bands (Table I).

Quenching Experiments. The relatively long lived ^{2}E excited state of *trans*-Cr(en)$_2$(NCS)$_2^+$ can undergo bimolecular deactivation if sufficient concentrations of suitable quenchers are present in solution. Some aspects of these quenching processes, including the reaction of ^{2}E with OH$^-$, have been previously discussed.[44] The results obtained in the present work (Figure 2) show that (1) phosphorescence quenching by Cr(CN)$_6^{3-}$ occurs by a dynamic mechanism; (2) Cr(CN)$_6^{3-}$ concentrations which cause an almost complete quenching of the phosphorescence emission leave unquenched a noticeable part of both photoreactions. The comparison between phos-
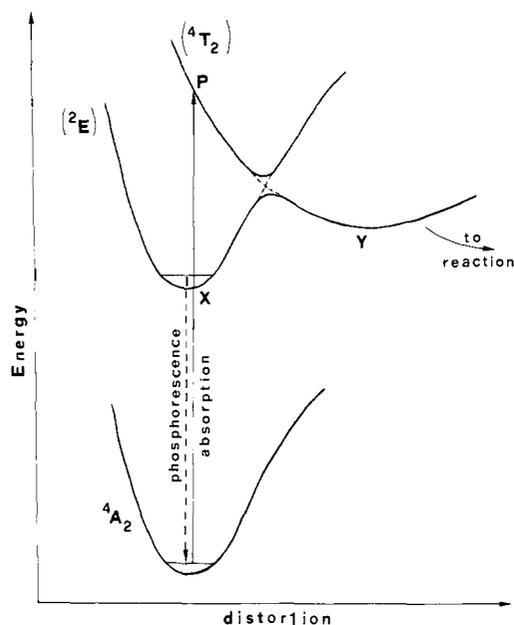
Figure 5. Schematic representation of the mixing of the doublet and quartet excited states owing to spin-orbit coupling (see text).
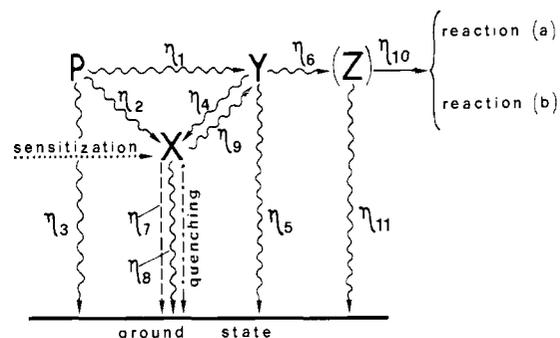

Figure 6. Schematic representation of the paths involved in the direct, sensitized, and quenched photochemistry. For the values of the efficiencies, see text.

phorescence and photolysis quenching is clearer plotting the data as in Figure 4. It is evident that on complete quenching of the phosphorescence emission (i.e., of the ^2E excited state), both photoreactions exhibit ~20% as unquenchable part.

Excited State Mechanism. Now we will try to answer the following questions, which are the traditional subjects of discussion in Cr(III) photochemistry: (1) Do photoreactions (a) and (b) originate from the same or different excited states? (2) Are both $^4T_2$ and ^2E chemically reactive? (3) Is back intersystem crossing from ^2E to $^4T_2$ an important process?

The unquenchable part of each photoreaction must originate from $^4T_2$ molecules which do not pass through ^2E. Thus, we can conclude that $^4T_2$ has to be, in some way, chemically reactive. For the quenchable part of the photoreactions there are two possible origins:[6,10,12,18] (1) direct reaction from ^2E; (2) reaction from $^4T_2$ after back intersystem crossing from ^2E ("delayed" $^4T_2$ reaction). It is important to note that the Φ_{NCS^-}/Φ_{H^+} ratio is the same for both the quenchable and unquenchable parts of the two photoreactions (Figure 4). Thus, if the quenchable parts derived from ^2E and the unquenchable parts derived from $^4T_2$, the two excited states would react with the same Φ_{NCS^-}/Φ_{H^+} ratio. This, however, is unlikely because ^2E and $^4T_2$ belong to different electronic configurations and are expected to exhibit different reactivities.[1-3] Thus, it seems likely that both photoreactions originate from the same excited state, that has to be $^4T_2$. In other words, the unquenchable and quenchable parts are prompt and delayed components of $^4T_2$ reactions. This implies that the back intersystem crossing from ^2E to $^4T_2$ has to be an important process. Quantitatively, it can be shown that in the above hypothesis the ratio between the quantum yields of the prompt and total photoreactions (0.2) is equal to $1 - \eta_{isc}\eta'_{isc}$, where η_{isc} and η'_{isc} are the efficiencies of forward and back intersystem crossing (Figure 3). As η_{isc} is about 0.8, η'_{isc} has to be about unity.[64,65]

A less traditional but probably more significant discussion can be done on the basis of the interpretative framework which has recently been proposed by Kane-Maguire et al.[42] When the complete (orbital + spin) wave functions are considered using the double group symmetry notations,[66,67] the ^2E state belongs to a G' representation and the $^4T_2$ state splits into $2G'$ + E_2' + E_3' irreducible components. As the spin-orbit operator is totally symmetrical, the ^2E and $^4T_2$ states may interact because of the common G' components, yielding an "avoided

crossing" situation.[68] According to this picture, we have a lower energy potential curve with two minima, X and Y (Figure 5). Upon excitation above the mixing region (e.g., to point P in Figure 5) the molecule can relax directly to either the X or Y minimum of the lower energy curve. Excitation in the tail of the $^4T_2$ band (i.e., below the mixing region) favors the relaxation to the Y minimum, with a consequent decrease of the quantum yield of phosphorescence[69] (Figure 1). The energy barrier between X and Y, in fact, can be low enough to allow interconversion,[70] but minimum Y has also an open channel to reaction, so that part of the molecules which reach Y directly from P undergo ligand substitutions (prompt or unquenchable photoreactions). The molecules which reach X directly from P can either emit (with extremely low efficiency) or go to Y where they can react (delayed or quenchable photoreactions) or come back to X.[71] Compared to excitation to point P, direct population of X via $Ru(bpy)_2(CN)_2$ sensitization increases the quantum yield of phosphorescence, but leaves unchanged the quantum yields of the photoreactions because practically all the molecules which populate X convert to Y from which they undergo reaction. On excitation to P, complete phosphorescence quenching (i.e., complete quenching of X) cannot quench that part of the reactions due to the molecules which relax directly from P to Y.[72] Whether the ligand substitution reactions occur directly from Y or from another intermediate (Z) is impossible to say. However, a concerted associative mechanism is most probable in view of the high degree of stereochemical change brought about by the photosubstitution reactions.[30,31] A quantitative discussion of this mechanism can be done on the basis of the scheme shown in Figure 6. The following relations can be obtained between mechanistic and experimental quantities:[55]

$$\Phi_{tot} = \eta_1\eta_6\eta_{10} + \eta_1 \frac{\eta_4\eta_9}{1 - \eta_4\eta_9} \eta_6\eta_{10}$$

$$+ \eta_2 \frac{1}{1 - \eta_4\eta_9} \eta_6\eta_{10} = 0.25$$

$$\Phi_{tot}^{unq} = \eta_1\eta_6\eta_{10} = 0.05$$

$$\Phi_{tot}^{sens} = \frac{\eta_9}{1 - \eta_4\eta_9} \eta_6\eta_{10} = 0.25$$

$$\frac{\Phi_p}{\Phi_p^{sens}} = \eta_2 + \eta_1\eta_4 = 0.8$$

where Φ_{tot} is the total photoreaction quantum yield (Φ_{NCS^-} + Φ_{H^+}) on direct excitation, Φ_{tot}^{unq} is its unquenchable part, Φ_{tot}^{sens} is the total limiting photoreaction quantum yield on sensitization conditions, and Φ_p and Φ_p^{sens} are the corresponding phosphorescence quantum yields. From these relations it follows that $\eta_9 \sim 1$, so that η_8 has to be negligible as is η_7. Assuming $\eta_3 = 0.0$ and taking the upper limiting value 0.6 for η_4, one gets $\eta_1 = 0.5$, $\eta_6\eta_{10} = 0.1$, $\eta_2 = 0.5$, $\eta_5 + \eta_6\eta_{11} = 0.3$.

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