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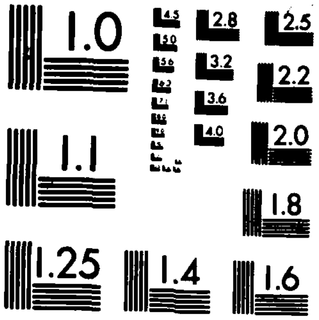

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The emission lifetime, $\tau$, and its temperature dependence is reported for aqueous $Cr(NH_3)_5(CN)^{2+}$ and trans-$Cr(NH_3)_4(CN)_2^+$. The $\tau$ values at 20 °C are 22 μs and 65 μs for pH 3 solution, respectively, and the corresponding activation energies are 11.2 kcal $mole^{-1}$ and 6.6 kcal $mole^{-1}$. The results are discussed in terms of previously suggested emission rules. The emission, presumably from the lowest doublet thexi state is in both cases quenched by hydroxide ion at about a diffusion controlled rate. In addition, the emission from $Cr(NH_3)_5(CN)^{2+}$ is (continued...)

11.2 kcal mole

6.6 kcal mole

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quenched by $Cr(CN)_6^{3-}$, the bimolecular quenching rate constant at 20 °C being $6.2\times10^8\ M^{-1}s^{-1}$. In the case of trans-$Cr(NH_3)_4(CN)_2^+$, the emission behavior is complicated by the accrual of thermal aquation product, and an emission lifetime of 205 ns appeared at 20 °C. On complete quenching of $Cr(NH_3)_5(CN)^{2+}$ by both $OH^-$ and $Cr(CN)_6^{3-}$, the photochemistry ($NH_3$ aquation) is only partly quenched, the unquenchable quantum yield being 27% of the yield in acid solution. The apparent activation energy (3 kcal $mole^{-1}$) and the isomeric distribution of photoproducts are the same for the quenchable and unquenchable photoreaction. Possible excited state mechanisms are discussed.

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by

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# Photochemistry and Photophysics of Aqueous $Cr(NH_3)_5(CN)^{2+}$ and trans-$Cr(NH_3)_4(CN)_2{}^+$

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## Abstract

The emission lifetime, τ, and its temperature dependence is reported for aqueous $Cr(NH_3)_5(CN)^{2+}$ and trans-$Cr(NH_3)_4(CN)_2{}^+$. The τ values at 20 °C are 22 μs and 65 μs for pH 3 solution, respectively, and the corresponding activation energies are 11.2 kcal mole$^{-1}$ and 6.6 kcal mole$^{-1}$. The results are discussed in terms of previously suggested emission rules. The emission, presumably from the lowest doublet thexi state is in both cases quenched by hydroxide ion at about a diffusion controlled rate. In addition, the emission from $Cr(NH_3)_5(CN)^{2+}$ is quenched by $Cr(CN)_6{}^{3-}$, the bimolecular quenching rate constant at 20 °C being $6.2 \times 10^8\ M^{-1}s^{-1}$. In the case of trans-$Cr(NH_3)_4(CN)_2{}^+$, the emission behavior is complicated by the accrual of thermal aquation product, and an emission lifetime of 205 ns appeared at 20 °C. On complete quenching of $Cr(NH_3)_5(CN)^{2+}$ by both $OH^-$ and $Cr(CN)_6^{3-}$, the photochemistry ($NH_3$ aquation) is only partly quenched, the unquenchable quantum yield being 27% of the yield in acid solution. The apparent activation energy (3 kcal mole$^{-1}$) and the isomeric distribution of photoproducts are the same for the quenchable and unquenchable photoreaction. Possible excited state mechanisms are discussed.

## Introduction

We report here on the thermally equilibrated doublet excited state (thexi state) emission behavior of two cyanoammine complexes of Cr(III). The thermal substitution kinetics have been reported for these complexes,[4,5] as well as their photochemistry,[6,7] so that both systems are well characterized. The present study is a continuation of earlier work on Cr(III) ammine complexes,[8] work which led to the suggestion that emission lifetimes tend to be governed by certain rules.

These rules are:

1. Emission lifetimes for $CrL_6^{n\pm}$ type complexes will be longer the greater the ligand field strength of the ligand L.

2. If two or more kinds of ligands are present, the emission lifetime will be relatively short if the pseudo-octahedral axis of smallest average ligand field strength contains the thermally labile ligand.

With only rare exceptions, emission from Cr(III) complexes is from the lowest state of doublet multiplicity, which we designate as $D_1^\circ$ to avoid symmetry-specific notations. The superscript zero indicates that the state is thermally equilibrated, or is a thexi state. The radiative lifetime of a $D_1^\circ$ state is typically in the millisecond range, as estimated from low temperature studies.[9] The above rules however, apply to emission from fluid solution in the vicinity of room temperature. Emission lifetimes are now typically in the ns to μs range. If we make the usual assumption that $k_r$, the radiative rate constant, is essentially temperature independent, then the decrease in emission lifetime, $\tau$, at higher temperatures must be due to the intervention of one or more of the other processes whereby $D_1^\circ$ can disappear. These other processes comprise nonradiative relaxation to the ground quartet state, $Q_0^o$, chemical reaction, and back intersystem crossing to the first excited quartet state, $Q_1°$. The respective rate constants for these processes are designated as $k_{nr}$, $k_{cr}$, and $k_{bisc}$. We thus assume that under room temperature conditions,

$$1/\tau = k_{nr} + k_{cr} + k_{bisc} \tag{1}$$

The systems whose behavior orginally suggested rule 2 above were mostly of the types $CrL_5X^{n+}$ and $CrL_4X_2^{n+}$, where X is of weaker ligand field strength than L, and is also the thermally labile ligand. Our interest here is in the behavior of complexes where X, while still the thermally labile ligand, is of greater ligand field strength than L. A more general interest, of course, was in the study of the photophysics of mixed cyanoammine complexes of Cr(III), a class not previously investigated.

Finally, there has been a continuing preoccupation with the question of whether $D_1°$ states may be chemically reactive (see refs. 10-18 and citations therein). There was the possibility that studies of quenching of emission and of photochemistry of cyanoammine complexes might add some new insights.

## Experimental

Materials.- $[Cr(NH_3)_5(CN)](ClO_4)_2$ and trans-$[Cr(NH_3)_4(CN)_2](ClO_4)$ were prepared by published methods,[4,5] and their purity was checked spectrophotometrically. That is, their uv-visible absorption spectra agreed within a percent or two with the published positions of the absorption maxima and the corresponding extinction coefficients, ε. $K_3[Cr(CN)_6]$ was prepared by a standard procedure,[19] and was recrystallized before use.

Buffer solutions were prepared from reagent grade chemicals. Dimethylformamide (DMF) was dried with 4 Å molecular sieve, and distilled at reduced pressure, under nitrogen atmosphere, before use.

Equipment and procedures. - Emission lifetimes measurements were made with the use of essentially the same equipment as that described earlier.[20] All solutions were filtered through 0.22 μm Millipore cellulose filters just before use, to eliminate artifacts due to dust. Emission spectra were obtained by means of a Perkin-Elmer 650-10S spectrofluorimeter. Emission yields were estimated by comparison of the corrected emission spectra with that of an optically matched solution of $Ru(2,2'\text{-bipyridine})_3^{2+}$, taking the yield of the latter to be 0.042 at 20 °C, with 436 nm excitation.[21] Light intensities for quantum yield determinations were measured by means of either a thermopile or reineckate actinometry.[22] Absorption spectra were obtained by means of either a Cary model 14 or a Hewlett-Packard model 8450 spectrophotometer.

Quantum yields for the photolysis of $Cr(NH_3)_5(CN)^{2+}$ were determined with 465 ± 4 nm excitation and using ca. 0.005 M solutions of complex, at an ionic strength of 0.10 M, adjusted with $NaClO_4$. In the pH 6-10 range, $H_2PO_4^-$ / $HPO_4^{2-}$, $B(OH)_3$ / $B(OH)_4^-$, or $NH_4^+$ / $NH_3$ buffers were used, the concentrations of which varied between $5\times10^{-3}$ and $5\times10^{-2}$ M, and were such that the buffer index was the same ($\beta = 5\times10^{-3}$) in all cases, allowing a $\Delta$pH of less than 0.05, during photoreaction. Samples of lower and higher pH's were prepared by use of $HClO_4$ or NaOH. Solutions with $Cr(CN)_6^{3-}$ as quencher, were also $5\times10^{-4}$ M in $HClO_4$. The irradiation cells, of 1-cm path length, were stoppered, to avoid reaction of atmospheric $CO_2$ with the basic samples. The temperature was maintained constant to within ± 0.1 °C, and photoconversion never exceeded 5%. Solutions photolyzed for the purpose of determining the product isomer distribution were simply adjusted to either pH 3 ($HClO_4$) of pH 12 (NaOH), and irradiated with 370 - 570 nm broad band light (CS 4-96 filter). The light source was a 250 W mercury arc lamp.

Emission lifetime measurements for $Cr(NH_3)_5(CN)^{2+}$ were carried out with 0.005-0.01 M solutions adjusted to pH 3.0 but not ionic strength buffered. Hydroxide ion quenching of the emission from this complex was determined in the presence of appropriately added NaOH solution. In the case of quenching by $Cr(CN)_6^{3-}$, pH 3.0 solutions were used, again without ionic strength buffering. Excitations were at 530 nm in the above experiments, and the emission was monitored at 680 nm. Emission intensities and intensity quenching were determined spectrofluorimetrically using solutions made up similarly to those for the lifetime studies, except that excitation was at 470 nm, where $Cr(CN)_6^{3-}$ does not absorb. Occasional duplication with Ar-purged samples showed no significant difference in the emission behavior of air-equilibrated and deaerated aqueous solutions.

Several pulse and steady-state irradiations were carried out in DMF solutions. Samples were 0.01 M and 0.005 M in complex respectively, *with or without added* $Cr(CN)_6^{3-}$. Excitation was again at 530 nm (pulsed) and 470 nm (continuous), with monitoring at both 680 nm and 800 nm.

Emission lifetimes for trans-$Cr(NH_3)_4(CN)_2^{+}$ were obtained with 353 nm excitation and 698 nm monitoring. Unbuffered water solutions were used for the temperature dependence studies. For the effect of pH on the acid and basic sides, 0.1 M potassium phthalate and 0.01 M $B(OH)_3$ / $B(OH)_4$ buffer mixtures were used respectively.

Analyses. - The photoreaction of $Cr(NH_3)_5(CN)^{2+}$ is one of ammonia aquation, and the rate of product formation was determined in one of several alternative ways, with good agreement. In the case of photolyses at initial pH's in the range 2.7 - 4.0, the irradiation was interrupted periodically and the pH measured to obtain the amount of ammonia release. In the case of irradiations at natural or basic pH's, an aliquot of standarized perchloric acid solution was added, sufficient to bring an unirradiated solution to pH 3.00. For an irradiated solution, the pH was higher and, from its value, the amounts of ammonia release could be determined.

Most of the results were rechecked with the use of an Orion Model 95-10 ammonia sensing electrode, connected to a Radiometer Model PHM 84 research pH meter. The sample pH was adjusted to ca. 12 by the addition of sodium hydroxide solution prior to measurement. Calibration was performed in parallel with each determination, by use of fresh ammonia ($NH_4Cl$-NaOH) standards.

An alternative spectrophotometric procedure was as follows. The changes in absorption spectrum that occur on irradiation of acidic solutions are not large enough to permit accurate monitoring of the amount of photolysis. The procedure was to add pH 9 $NH_4^+$ / $NH_3$ buffer to a photolyzed solution to convert the product to $Cr(NH_3)_4(OH)(CN)^+$. The optical density at 390 nm is now near a maximum for the product, and at a *minimum for the* starting complex, thus permitting relatively easy determination of the amount of photolysis.

It should be noted that irradiations in the more basic media yielded solutions that were not stable, but became cloudy after 10 - 20 min. in the dark, with increase in pH. Eventually, a blue-grey solid would precipitate out. The spectrophotometric analysis of such solutions had therefore to be carred out expeditiously. If, however, the solutions were acidified immediately after photolysis, the sequence of absorption spectra for successive photolyses showed good isosbestic points and essentially the same ones as previously reported.[6]

Isolation of the photoaquation products, cis and trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, was accomplished by ion-exchange chromatography with 4x1 cm columns of

Sephadex SP-C25 cationic resin in the sodium form, as previously reported.[6] Photolyzed alkaline solutions were loaded onto the columns, whereas acidic samples were brought to pH 11.7 with sodium hydroxide solution before being processed. Elution by 0.10 M $NaClO_4$ at pH 11.7 (NaOH) separated the deprotonated plus one charged products from the dipositive starting complex. The eluates were acidified to pH ca. 0 with $HClO_4$, and allowed to stand in the dark at room temperature for one hour, so as to allow complete conversion of the aquo-cyano isomers to the corresponding $Cr(NH_3)_4(H_2O)_2^{3+}$ species. Thermal aquation of coordinated cyanide is entirely stereoretentive.[5] The ligand field absorption spectra of these mixtures were then recorded, and the chromium content was determined spectrophotometrically at 374 nm ($\varepsilon = 4760\ M^{-1}cm^{-1}$) after oxidation to chromate by means of alkaline hydrogen peroxide.

The isomeric distribution of the diaquotetraammine complexes, and hence that of the photoproducts was found by fitting the above absorption spectra with linear combinations of those for trans- and cis-$Cr(NH_3)_4(H_2O)_2^{3+}$. A least-squares minimization procedure was applied, by use of an HP 9825 B desk computer connected with a plotter, which allowed direct reading from the spectrophotometer charts, including base-line corrections, if needed. This analysis could be extended routinely to over 120 wavelengths. A control of the quality of the result was provided by comparison of the chromium concentration given by the fitting with that determined by chemical analysis. The two independent results generally agreed to within ± 3%.

## Results

Emission and emission quenching of $Cr(NH_3)_5(CN)^{2+}$. - The $D_1°$ emission from aqueous $Cr(NH_3)_5(CN)^{2+}$ is relatively long, $\tau = 22.4 \pm 0.8\ \mu s$ at 20 °C. Two independent series of determinations of the temperature dependence were made, involving three or four separate measurements at each temperature, with the results shown in Figure 1. We find $1/\tau = 1.1\text{x}10^{13} \exp(-5650/T)\ s^{-1}$, corresponding to an apparent activation energy of 11.2 ± 0.3 kcal $\text{mole}^{-1}$. The emission yield at 20 °C is 0.0020 for 436 ± 3 nm excitation.[23]

Both the absorption and the emission spectra of $Cr(NH_3)_5(CN)^{2+}$ exhibit vibrational fine structure in the 640-720 nm region, as shown in Figure 2. The absorption fine structure is found on the tail of the first quartet-quartet absorption band, presumably corresponding to the $Q_0^0$-$D_1$ transition, while that for the emission is found on a broad band which has its maximum at 680 nm. The separations between features in the two spectra are somewhat similar, suggesting a common type of origin. Also, however, the considerable overlap in the 650-680 nm region suggests that hot bands may be involved. It is possible that different components of the $D_1°$ state are involved.

The emission is quenched by hydroxide ion, and the relevent Stern-Volmer type plot is shown in Figure 3.[24] The data, for 20 °C, give a bimolecular quenching rate constant, $k_q$, of $6.2\text{x}10^9\ M^{-1}s^{-1}$, as defined by the equation

$$I°/I = \tau°/\tau = 1 + k_{SV}[Q],\quad k_{SV} = \tau°k_q \qquad (2)$$

Here, I denotes emission yield and superscript zero denotes value for quencher concentration [Q] equal to zero. This value of $k_q$ is at about the diffusion limited value. There was also quenching by $Cr(CN)_6^{3-}$. Here again, emission intensity and emission lifetime quenching were determined and, as shown in Figure 4, the results of the two types of measurements are in agreement. The calculated bimolecular quenching rate constant is $6.2\text{x}10^8\ M^{-1}s^{-1}$ for 20 °C.

Although oppositely charged ions are involved in the case of quenching by $Cr(CN)_6^{3-}$, it is unlikely that static quenching through ion pair formation was important because of the agreement between the I°/I and τ°/τ plots. Also, the highest $Cr(CN)_6^{3-}$ concentration used (able to quench 94% of the emission) was only 13% of the $Cr(NH_3)_5(CN)^{2+}$concentration, which puts this limit on the maximum possible degree of ion pairing of the latter species.

Some luminescence measurements were carried out in DMF solution, where $Cr(CN)_6^{3-}$ is known to emit,[25,26] in contrast to its behavior in aqueous media. The lifetime of the cyanopentaammine complex is, in this solvent, 18.9 ± 0.7 μs at 20 °C. As shown in Figure 5, the decrease in the emission intensity of $Cr(NH_3)_5(CN)^{2+}$ is accompanied by a progressive rise in that of the $Cr(CN)_6^{3-}$ phosphorescence at 800 nm. Both phenomena obey Stern-Volmer kinetics, $k_{SV} \simeq 3x10^4\ M^{-1}$ at 20 °C. Sensitized emission of $Cr(CN)_6^{3-}$ was also observed following pulse excitation at 530 nm, where only $Cr(NH_3)_5(CN)^{2+}$ absorbs. A $4x10^{-3}$ M solution of the former complex completely quenches the emission of the latter one, and the induced 800 nm emission from $Cr(CN)_6^{3-}$ decays exponentially with a lifetime of 80 μsec. This τ value is much smaller than the 540 μs reported for the complex alone in air-equilibrated DMF.[25] Evidently, reverse energy transfer takes place, as has been demonstrated for other sensitizer Cr(III) complexes.[27]

Quenching of photochemistry of $Cr(NH_3)_5(CN)^{2+}$. - The photochemistry has been reported previously.[6] It consists entirely of ammonia aquation, in aqueous acidic solution, and with a wavelength-independent quantum yield of 0.37 ± 0.01 at 20 °C.[28] The yield, ϕ, is partially quenched on quenching the emission, dropping to a limiting value, $\phi_{lim}$, of 0.10 ± 0.01 at pH's above 11, that is, under conditions of complete emission quenching. The results are summarized in Table I. For pH's between 8 and 10, the plot of $\phi°/\phi°$ vs. $\tau/\tau°$ is essentially linear, as would be expected if quenching and photochemistry were in partial competition. From the intercept,[29] see Figure 6, 27% of the yield is unquenchable.

The plot of Figure 6 has an upper right intercept which is not unity. This reflects the fact that, initially, the luminescence appears to be quenched more efficiently (by 10-15%) than the photoreaction, That is, while the quenching of emission intensity and of $\tau$ begins around pH 6.5, the decrease in $\phi$ begins only around pH 7.5. Above this pH, the changes in the two quantities become parallel.

Temperature dependence data are included in Table I. The $\phi$ values shown an apparent activation energy of 3.3 ± 0.3 kcal $\text{mole}^{-1}$ under pH 3.3 conditions, and one of 3.0 ± 0.3 kcal $\text{mole}^{-1}$ at pH 11.7, as illustrated in Figure 1. These two values are the same within experimental error, indicating that there is no significant change in temperature behavior under quenching conditions.

There was also quantum yield quenching by $Cr(CN)_6^{3-}$. The data are given in Table I and are plotted in Figures 4 and 6. The latter gives, within experimental error, the same fraction of unquenchable yield as was found for $OH^-$ quenching. Virtually none of the 465 nm incident radiation was absorbed by $Cr(CN)_6^{3-}$.

Finally, it was of interest to determine to what extent the distribution of photoproduct isomers was sensitive to quenching. Four independent determinations were carried out in both acid and basic medium. Photolysis in $1\times10^{-3}$M $HClO_4$ solution yielded 28 ± 5% trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (and 72% cis isomer).[30] Under conditions of complete quenching of emission, 0.01 M NaOH solution, we found 29 ± 3% trans isomer, or essentially no change.

Table I

Quantum Yields for $NH_3$ Photoaquation of $Cr(NH_3)_5(CN)^{2+}$ in Aqueous Solution.[a]

| temp, °C | pH | $[OH^-]$ | $[Cr(CN)_6^{3-}]$ | $\phi_{NH_3}$ [b] |
|---|---|---|---|---|
| 25 | 3.3 | | | 0.410 ± 0.020 (4) |
| 20 | 3.3 | | | 0.371 ± 0.014 (7) |
| 14 | 3.3 | | | 0.325 ± 0.020 (5) |
| 4 | 3.3 | | | 0.270 ± 0.010 (5) |
| 20 | 6.49 | $2.8x10^{-8}$ | | 0.370 ± 0.010 (3) |
| 20 | 6.82 | $6.0x10^{-8}$ | | 0.372 ± 0.010 (2) |
| 20 | 7.35 | $2.0x10^{-7}$ | | 0.373 ± 0.010 (3) |
| 20 | 7.79 | $5.6x10^{-7}$ | | 0.358 ± 0.010 (3) |
| 20 | 8.44 | $2.5x10^{-6}$ | | 0.340 ± 0.010 (4) |
| 20 | 8.79 | $5.6x10^{-6}$ | | 0.290 ± 0.010 (4) |
| 20 | 8.92 | $7.5x10^{-6}$ | | 0.276 (1) |
| 20 | 9.39 | $2.2x10^{-5}$ | | 0.216 ± 0.010 (3) |
| 20 | 9.44 | $2.5x10^{-5}$ | | 0.214 (1) |
| 20 | 9.62 | $3.8x10^{-5}$ | | 0.175 (1) |
| 20 | 10.04 | $9.9x10^{-5}$ | | 0.131 ± 0.010 (2) |
| 20 | 10.67 | $4.2x10^{-4}$ | | 0.110 ± 0.010 (2) |
| 20 | 11.67 | $4.2x10^{-3}$ | | 0.104 ± 0.005 (4) |
| 25 | 11.67 | | | 0.117 ± 0.003 (2) |
| 14 | 11.67 | | | 0.094 ± 0.005 (4) |
| 4 | 11.67 | | | 0.081 ± 0.001 (2) |
| 20 | 13.0 | | | 0.100 (1) |
| 20 | 3.3 | | $9.1x10^{-5}$ | 0.250 (1) |
| 20 | 3.3 | | $1.7x10^{-4}$ | 0.219 (1) |
| 20 | 3.3 | | $3.5x10^{-4}$ | 0.179 (1) |
| 20 | 3.3 | | $2.3x10^{-3}$ | 0.114 (1) |
| 20 | 3.3 | | $8.0x10^{-3}$ | 0.111 ± 0.004 (4) |

[a] Conditions: irradiation at 465 nm; $\mu = 0.10$; $f_{OH^-} = 0.755$; $K_w = 6.77x10^{-15}$ at 20.0 °C. [b] Number of determinations in parentheses.

Emission and emission quenching of trans-$Cr(NH_3)_4(CN)_2^+$. - We find the emission lifetime in pH 5 aqueous solution to be 44 ± 4 μs at 20 °C. The temperature dependence is included in Figure 1, and leads to an apparent activation energy of 6.6 ± 0.5 kcal $mole^{-1}$ and a pre-exponential factor of $1.9x10^9$ $s^{-1}$. Both values, and especially the latter one, are much smaller than for $Cr(NH_3)_5(CN)^{2+}$.

A complication developed with acidic solutions. The complex undergoes a moderately rapid, acid catalyzed aquation,[5] and in emission studies around pH 3, it was difficult to avoid the presence of some of the thermal aquation product, trans-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ (species B). Thus at pH 3.10, the emission decay was biphasic, and the appearance of the decay traces changed with the time of standing of the solution. For a $3.7x10^{-3}$M solution having undergone 4% thermal aquation, there was a weak fast component to the decay, and a slow component showing a lifetime of 60 μs. At about 50% thermal aquation, the fast component, now quite apparent, showed a lifetime of 205 ns, while the lifetime of the slow component has dropped to 35 μs. At yet higher degrees of thermal reaction, the fast component remained at 205 ns lifetime, while the slow component lifetime continued to decrease in value. Thus at 82% aquation, $\tau$ for the slow component had dropped to 28 μs. The behavior of this component obeyed the equation $1/\tau = 0.71x10^7 [b] + 1.53x10^4$, with $\tau$ in s and [B] in M units. Extrapolation to zero content of thermal aquation product gives the lifetime of pure trans-$Cr(NH_3)_4(CN)_2^+$ as 65 μs at 20 °C, for pH 3.10 (phthalate buffering).

Note that there appears to be a pH dependence of the emission lifetime in acidic solutions. In water at pH 5.5 and with phthalate buffering at pH 5.0, the previously quoted value of 44 μs was observed, with no indication of biphasic behavior. With buffered solutions of pH 4.0 and 3.5, the $\tau$ values observed were 58 and 61 μs, respectively.

There was also some concentration dependence of the longer lifetime component in pH 4.0 phthalate buffered solution. For fresh samples, the lifetime dropped from 67 μs for $0.5\times10^{-3}$ M solution to 56 μs for $3.8\times10^{-3}$ M solution, the progression in $\tau$ values being a steady one for a series of intermediate concentrations.

In basic solution, no biphasic emission behavior was observed, but there was lifetime quenching. The data are included in Figure 3, and lead to a $k_q$ value of $2.0\times10^{9}$ $M^{-1}$ $s^{-1}$ at 20 °C; a plot of $1/\tau$ vs. $[OH^-]$ gives $\tau°$ as 41.6 μs, as compared to the value of 44 μs for the measurements at pH 5.0, but within the error range of the latter. No study was made of possible quenching of photochemistry.

## Discussion

Emission rules. - Our immediate interest was in whether the emission rules cited in the Introduction were indeed predictive for new systems. The weak field axis is the ammonia-ammonia one for both $Cr(NH_3)_5(CN)^{2+}$ and trans-$Cr(NH_3)_4(CN)_2^{+}$. This axis does not contain the thermally labile ligand, which is cyanide in both cases,[4,5] and rule 2 therefore predicts that the emission lifetimes in room temperature solution should be relatively long. This is indeed the case. The lifetimes of 22 and 65 μs at 20 °C are among the longer ones known for Cr(III) complexes.

Emission quenching.- The kinetic data for the various quenching experiments with $Cr(NH_3)_5(CN)^{2+}$ are summarized in Table II. It is by now not surprising that $OH^-$ ion quenches the emission from both of the above complexes. Hydroxide quenching has been reported in the case of $Cr(NH_3)_6^{3+}$,[31] $Cr(en)_3^{3+}$ (en = ethylenediamine),[32,33] $Cr(phen)_3^{3+}$

**Table II.** Quenching Parameters for the Photolysis and the Luminescence of $Cr(NH_3)_5(CN)^{2+}$ in Aqueous Solution at 20 °C.

| parameter | quencher | |
|---|---|---|
| | $OH^-$ | $Cr(CN)_6^{3-}$ |
| $k_{SV}$ from $\frac{\phi_o-\phi_{lim}}{\phi-\phi_{lim}}$ $(M^{-1})$ | $(7 \pm 1)x10^4$ | $(8.3 \pm 0.5)x10^3$ |
| $k_{SV}$ from $I_o/I$ $(M^{-1})$ | $(1.2 \pm 0.1)x10^5$ | $(1.1 \pm 0.1)x10^4$ |
| $k_{SV}$ from $\tau_o/\tau$ $(M^{-1})$ | $(1.3 \pm 0.1)x10^5$ | $(1.2 \pm 0.1)x10^4$ |
| $k_q$ from $\tau_o/\tau$ $(M^{-1}s^{-1})$ | $(6.2 \pm 0.3)x10^9$ | $(6.2 \pm 0.5)x10^8$ |

(phen = 1,10-phenanthroline),[34] trans-$Cr(en)_2(NCS)_2^+$,[35] as well as for $Rh(NH_3)_5X^{2+}$ (X = Cl, Br).[36,37] As has been noted,[31,36] the quenching mechanism may be one of excited state proton transfer since neither excitation energy nor electron transfer quenching seems likely for $OH^-$ ion. The process in our case seems specific for hydroxide ion, since the same degree of quenching was observed for $Cr(NH_3)_5(CN)^{2+}$ for unbuffered and for variously buffered solutions of a given pH. This could simply be a matter of kinetics, a Grotthus-type mechanism allowing encounters to occur much more frequently with $OH^-$ ion than with basic solutes at the same concentration. We did not, however, test $CO_3^{2-}$ ion, which was a quencher for $Rh(NH_3)_5Cl^{2+}$ emission.[36]

The quenching by $Cr(CN)_6^{3-}$ is undoubtedly due to excitation energy transfer. This mechanism is directly evidenced by the experiments in DMF solution in that induced 800 nm emission, characteristic of $Cr(CN)_6^{3-}$, is observed. Such emission would not be expected to be observable in aqueous media because of the short lifetime of $D_1^\circ$ $Cr(CN)_6^{3-}$ in this solvent.[38] Quite similar excitation energy transfer between Cr(III) ammines and $Cr(CN)_6^{3-}$ has been reported previously.[27] Such systems can be analyzed by means of a set of coupled first order rate equations.

The biphasic nature of the emission decay in the case of acidic solutions of trans-$Cr(NH_3)_4(CN)_2^+$, A, containing various concentrations of thermal aquation product, B, is likely also due to excitation energy transfer. We could assign the 205 ns decay time to the $D_1^\circ$ state of B.[39] Coupling due to reversible excitation energy transfer[27] is expected to decrease the lifetime for A* with increasing concentration of B, as observed. This is because the rate constants for forward and reverse excitation energy transfer would depend on the B and A concentrations, respectively. Similarly, given some B in the system, an increase in the initial concentration of A would again lead to a decrease in the observed A* lifetime, as is found.

It remains to consider why the emission lifetime of A showed as 44 μs in pH 5 solution, but rose to 65 μs at pH 3. The effect was not investigated in any detail. However, one possibility is that protonation of A occurs in this pH region, AH* having the 65 μs lifetime. A perhaps more likely possibility is that some of the thermal aquation product B was present in A as an initial impurity. The $pK_a$ of B is 5.5,[5] so that at the higher pH's, B would be present at least partly in the deprotonated form, <u>trans</u>-$Cr(NH_3)_4(OH)(CN)^+$, and we have observed that this species has a short emission lifetime. Excitation energy transfer lifetime mixing would then have the effect of reducing the apparent $\tau$ for A.

<u>Excited state kinetic scheme</u>. - Our simple excited state scheme for a $d^3$ system is shown in Ref. 15. We take $Q_1°$ to be more distorted than $D_1°$ because of the presence of an antibonding electron in the former case, in $O_h$ symmetry. (Such a presence could lead to considerable departure from even pseudo octahedral symmetry and $Q_1°$ could alternatively be regarded as an energetic isomer of $Q_0^0$.) The scheme considers only the lowest doublet and quartet thexi states, thus ignoring possible splitting of states due to reduction in symmetry.

As a general statement, chemical reaction may occur from either $Q_1°$ or from $D_1°$, and we can write

$$\phi = f_{pisc}\phi_{D_1°} + (1 - f_{pisc})\phi_{Q_1°} \qquad (3)$$

where $f_{pisc}$ is the fraction of initially produced Franck-Condon quartet excited states which undergo prompt intersystem crossing to $D_1°$. The quantities $\phi_{D_1}°$ and $\phi_{Q_1}°$ are the yields of product formation from the two states. We neglect, at this level of discussion, any prompt reaction, that is, reaction occuring before thermal equilibration to $Q_1°$ or $D_1°$.

A second general possibility is that the unquenchable portion of the yield is artifactual in the sense that the quenching encounter itself is reactive. This explanation is not implausible in the case of hydroxide quenching since, if the mechanism were one of excited state proton transfer, the product complex, $Cr(NH_3)_4(NH_2)(CN)^+$, might well be quite reactive. The same situation would presumably apply in the case of trans-$Cr(NH_3)_4(CN)_2^+$. However, the unquenchable quantum yield is about the same for both hydroxide ion and $Cr(CN)_6^{3-}$ quenched systems. Since the quenching mechanisms are most likely quite different in the two cases, it is improbable that both types of quenching encounters would lead to the same degree of reaction.

Returning, therefore, to the first category of explanation, it remains to consider whether the actual process is one of direct $D_1°$ reactivity, or one of back intersystem crossing followed by $Q_1°$ reaction. A preliminary point is that the emission from $D_1°$ is activated by 11.2 kcal $mole^{-1}$ and 6.6 kcal $mole^{-1}$ for the mono- and dicyano complexes, respectively. Referring to Eq. (1), it seems unlikely that $k_{nr}$ is emission lifetime controlling in view of this appreciable temperature dependence. As has been discussed earlier, it seems likely that at low temperatures, $k_{nr}$ is indeed emission lifetime controlling.[20] The temperature dependence of $k_{nr}$ seems generally to be small for Cr(III) ammines with the consequence that the more temperature dependent $k_{cr}$ or $k_{bisc}$ quantities become the dominant term in Eq. (1) at room temperature. Either process could be activated in the 7-11 kcal $mole^{-1}$ range. The $D_1°$ lifetimes for our complexes are long enough to permit this degree of activation; alternatively put, the frequency factors are not unreasonably large. Also, either process could be assigned such an activation energy from the molecular point of view. Chemical reaction from $D_1°$ could certainly be activated. In ligand field theory, the $^2E_g$ state in $O_h$ symmetry has one unpaired and two paired electrons in the non-bonding set of orbitals. The actual orbital population is uniform, however, due to the linear combination of wave functions that is involved.[40] This orbital population could be polarized, however, by an approaching entering ligand, to allow for a seven-coordinated reaction intermediate--a process which should require some activation. Alternatively, if the mechanism were one of ligand dissociation, the process should again require some activation.

The other possibility of back intersystem crossing could show a 6-11 kcal mole$^{-1}$ activation either because this is the $Q_1°$-$D_1°$ energy difference or because of activation energy for a process requiring both a change in molecular geometry and in spin. In the present case, incidentally, it is difficult to estimate the $Q_1°$-$D_1°$ energy gap because of the considerable overlap of the vibronic features of the absorption and emission bands.

The fact that the photoreaction mode is one of ammonia aquation for both the quenchable and the unquenchable components is not helpful. This mode would be predicted from rationalization of the emission rules,[8] if $k_{cr}$ were important, and from the photolysis rules if $k_{bisc}$ followed by reaction from $Q_1°$ were important.[6,7] The observation that the temperature dependence of $\phi$ is about the same for both the quenchable and the unquenchable portion, in the case of $Cr(NH_3)_5(CN)^{2+}$, and smaller than for $\tau$, namely 3 kcal mole$^{-1}$ vs. 11 kcal mole$^{-1}$, is suggestive although not diagnonostic. One explanation is that $f_{pisc}$ has little temperature dependence, essentially all of $D_1°$ back intersystem crosses to $Q_1$,[41] and that $\phi_{Q_1}°$ has a 3 kcal mole$^{-1}$ temperature dependence. In the other scenario, all quenchable reaction is from $D_1°$, and $\phi_{D_1}°$ is now unity.[41] The temperature dependence of the quenchable $\phi$ would now be assigned to $f_{pisc}$ and for the unquenchable yield to still have a temperature dependence of 3 kcal mole$^{-1}$ (and not

-3 kcal mole$^{-1}$), the apparent activation energy for $\phi_{Q_1}{}^\circ$ would have to be 6 kcal mole$^{-1}$. The above considers only the extremes; there is no new insight, however, in postulating mixed situations where $k_{cr}$ and $k_{bisc}$ are commensurate in value.

Finally, it is again suggestive although not absolutely diagnostic that the isomer ratio of the photoproduct is the same for both the quenchable and the unquenchable contributions, in the case of $Cr(NH_3)_5(CN)^{2+}$. This implies either that all reaction is from a single reactant, which must then be $Q_1{}^\circ$, or that the mechanisms of $D_1{}^\circ$ and $Q_1{}^\circ$ reaction involve similar transition states. The former case is the more appealing, being simpler. In the possibly related case of trans-$Cr(cyclam)(CN)_2{}^+$ it has likewise been difficult to decide between $^2E$ reactivity and back intersystem crossing.[17]

There remain minor aspects suggesting complexity. In the case of $Cr(NH_3)_5(CN)^{2+}$, there is a decrease in emission lifetime in the region of pH 6-8, after which linear Stern-Volmer quenching by hydroxide ion is observed, with the same $k_{SV}$ as for intensity quenching. In acid solution, the lifetime is 22 μs, while that from the extrapolated plot of $1/\tau$ vs. [OH] is 16 μs. Secondly, $k_{SV}$ as found from the plot of $(\phi^\circ - \phi_{lim})/(\phi - \phi_{lim})$ is less than the value determined from lifetime or emission quenching, for both $OH^-$ and $Cr(CN)_6{}^{3-}$ quenchers (see Table II).[42] Lastly, as shown in Figure 6, the plot of $\phi/\phi^\circ$ vs. $\tau/\tau^\circ$ does not quite intercept at the upper left corner, as it should. Reactive quenching would not explain these effects. There is a possibility of some undetected formation of the linkage isomer $Cr(NH_3)_5(NC)^{2+}$ in the preparation and conceivably this could account for the above observations. One indication of the presence of such isomer is that there is some initial curvature at short times in the first order plot of the thermal aquation reaction in acid solution.[43]

## Acknowledgments

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## References and Notes

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(41) Were this not so, then $k_{nr}$ would have to be a competitive exiting process for $D_1°$ ($k_{cr}$ being neglected in this scenario), that is, competitive both to $k_r$ and to $k_{bisc}$. The quenchable yield should then show something like the 11 kcal mole$^{-1}$ temperature dependence for emission, contrary to observation; also the 11 kcal mole$^{-1}$ apparent activation energy for emission would have to be assigned to $k_{nr}$ which seem unreasonable. In the alternative scenario, similar difficulties arise if $k_{cr}$ is not dominant, that is, if $\phi_{D_1}°$ is not essentially unity.

(42) Possibly, the different ionic strength conditions of the two sets of experiments accounts for the difference in $k_{SV}$ values.

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## Legends for the Figures

Figure 1. Temperature dependence of emission and photochemistry. 0- emission lifetimes at pH 5.0 for $Cr(NH_3)_5(CN)^{2+}$; □ - same for <u>trans</u>-$Cr(NH_3)_4(CN)_2^{+}$. Ammonia photoaquation yields for $Cr(NH_3)_5(CN)^{2+}$: Δ - pH 3.3; ▲ - pH 11.7.

Figure 2. Doublet absorption region (left scale) and emission spectrum (right scale) for $Cr(NH_3)_5(CN)^{2+}$ in acidic aqueous solution.

Figure 3. Stern Volmer type plot for hydroxide quenching of emission at 20 °C. $Cr(NH_3)_5(CN)^{2+}$: 0 - $\tau°/\tau$ and ● - $I°/I$. <u>Trans</u>-$Cr(NH_3)_4(CN)_2^{+}$: □ - $\tau°/\tau$.

Figure 4. Stern-Volmer type plot of quenching of $Cr(NH_3)_5(CN)^{2+}$ by $Cr(CN)_6^{3-}$ in aqueous solutions at pH 3.3 and 20 °C. 0 - emission intensity; ● - emission lifetime; □ - ammonia photoaquation yield.

Figure 5. Emission spectra at 20 °C of $Cr(NH_3)_5(CN)^{2+}$, A, and $Cr(CN)_6^{3-}$, B, upon 470 nm excitation of $5.0 \times 10^{-3}$ M A in DMF, in the presence of increasing concentrations of B. The sequence of concentrations of B is : (0), none; (1), $9.8 \times 10^{-6}$; (2) $2.0 \times 10^{-5}$; (3), $4.9 \times 10^{-5}$; (4), $9.8 \times 10^{-5}$; (5), $1.5 \times 10^{-4}$; (6), $2.0 \times 10^{-4}$ M.

Figure 6. Quenching of ammonia photoaquation of $Cr(NH_3)_5(CN)^{2+}$ <u>vs</u>. emission quenching, under the same conditions. Quenchers are: 0-$OH^-$; ●-$Cr(CN)_6^{3-}$.

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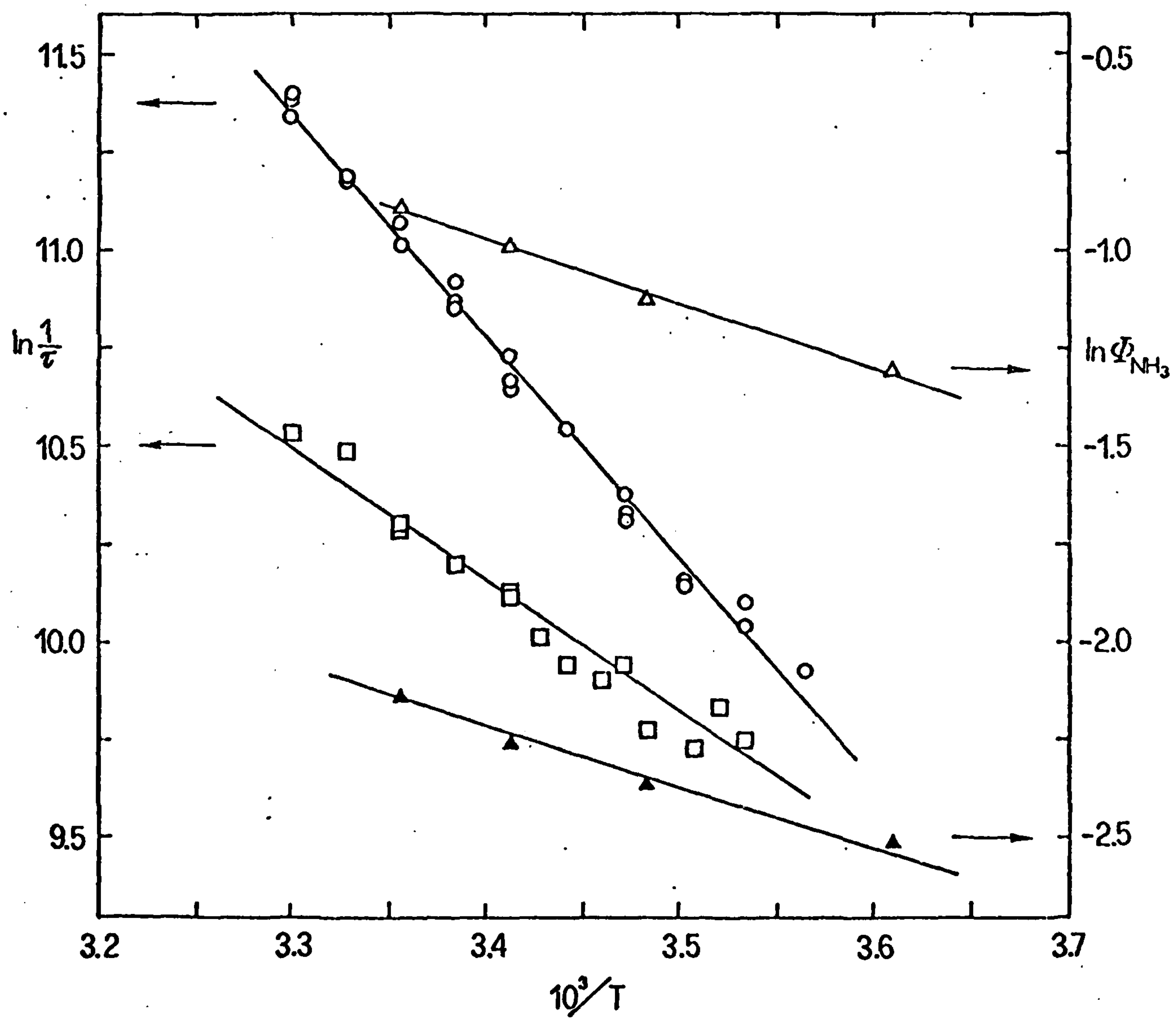
11.5
11.0
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9.5
$\ln \frac{1}{\tau}$
-0.5
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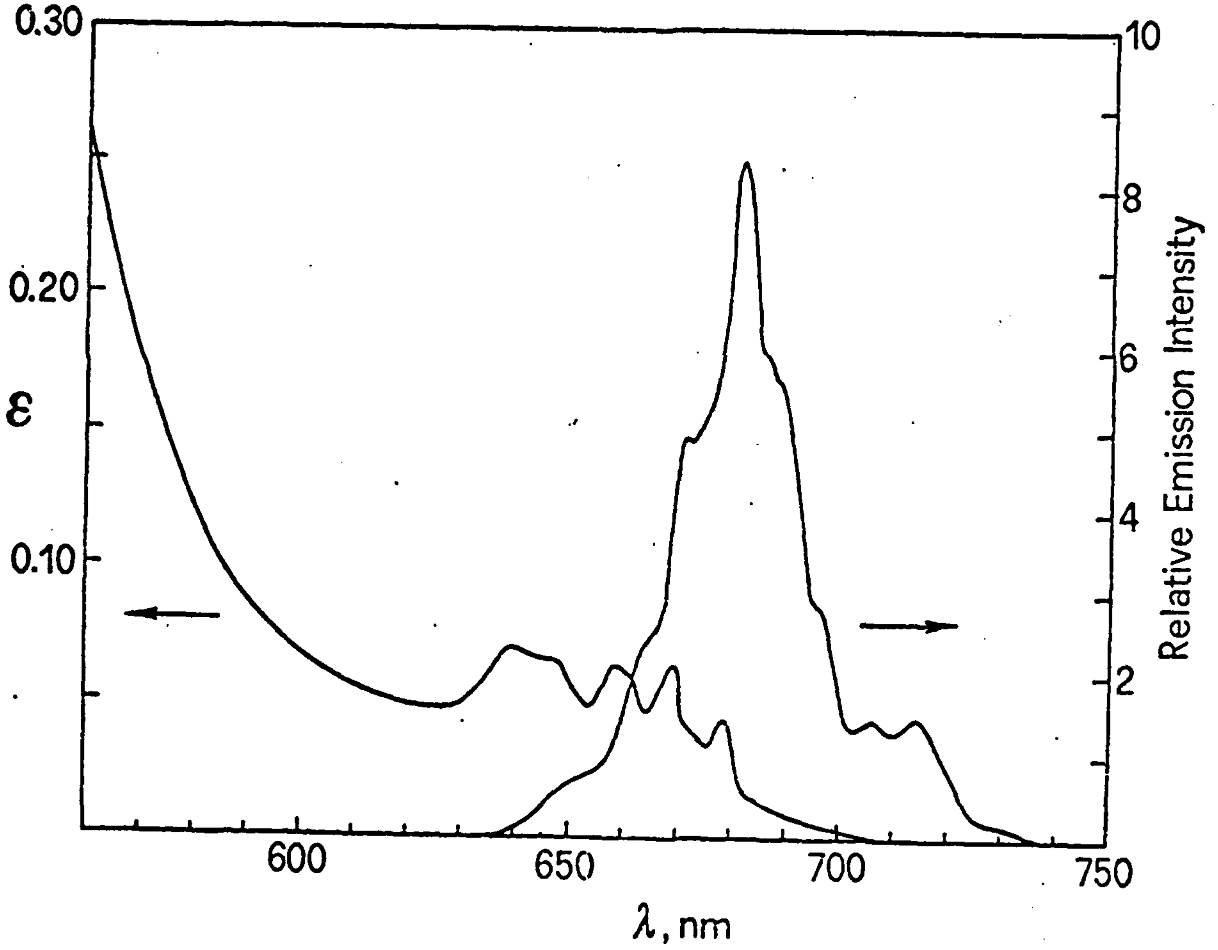
0.30
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4
2
Relative Emission Intensity
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700
750
λ, nm

Fig. 1

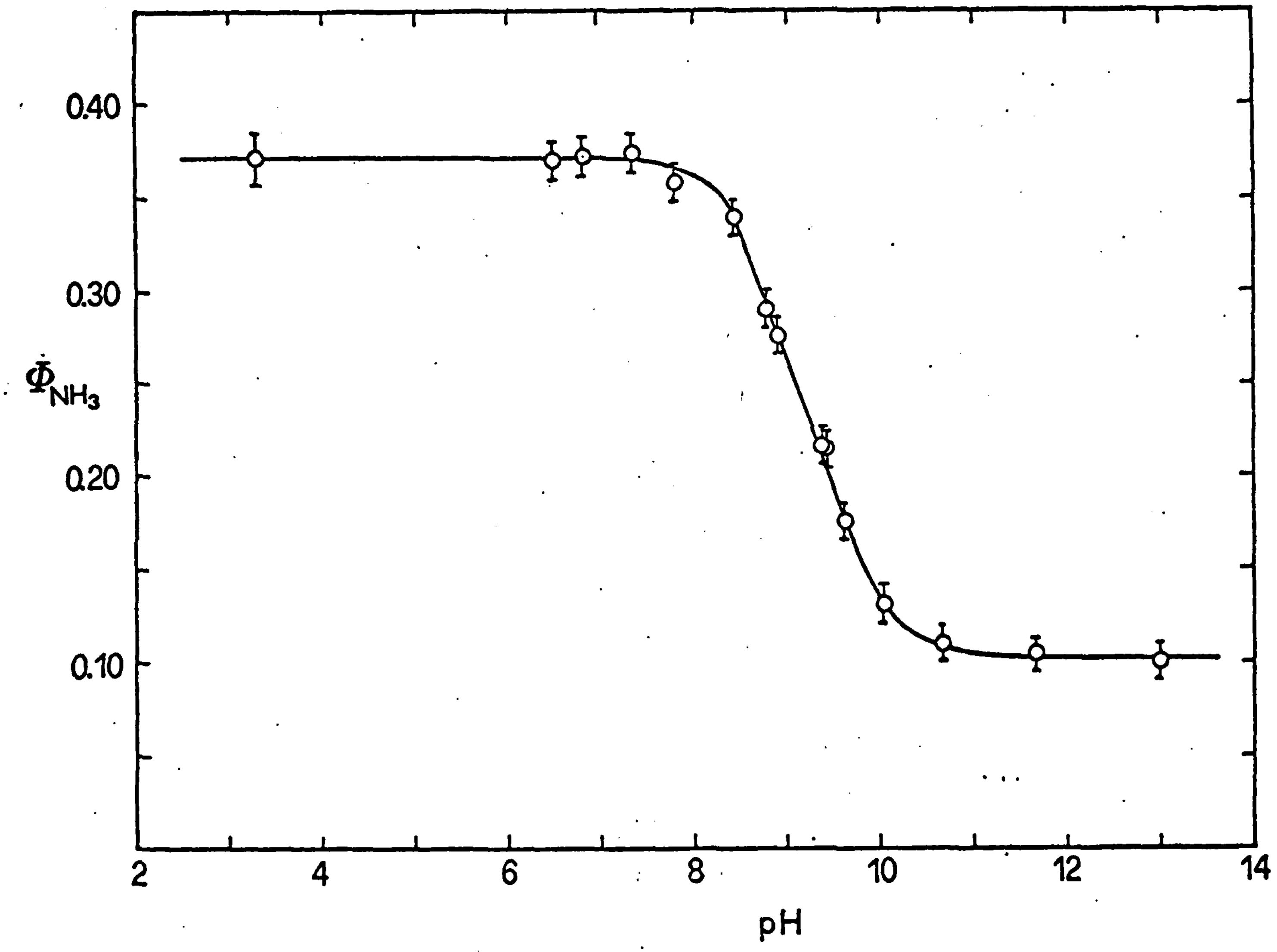


Fig. 5

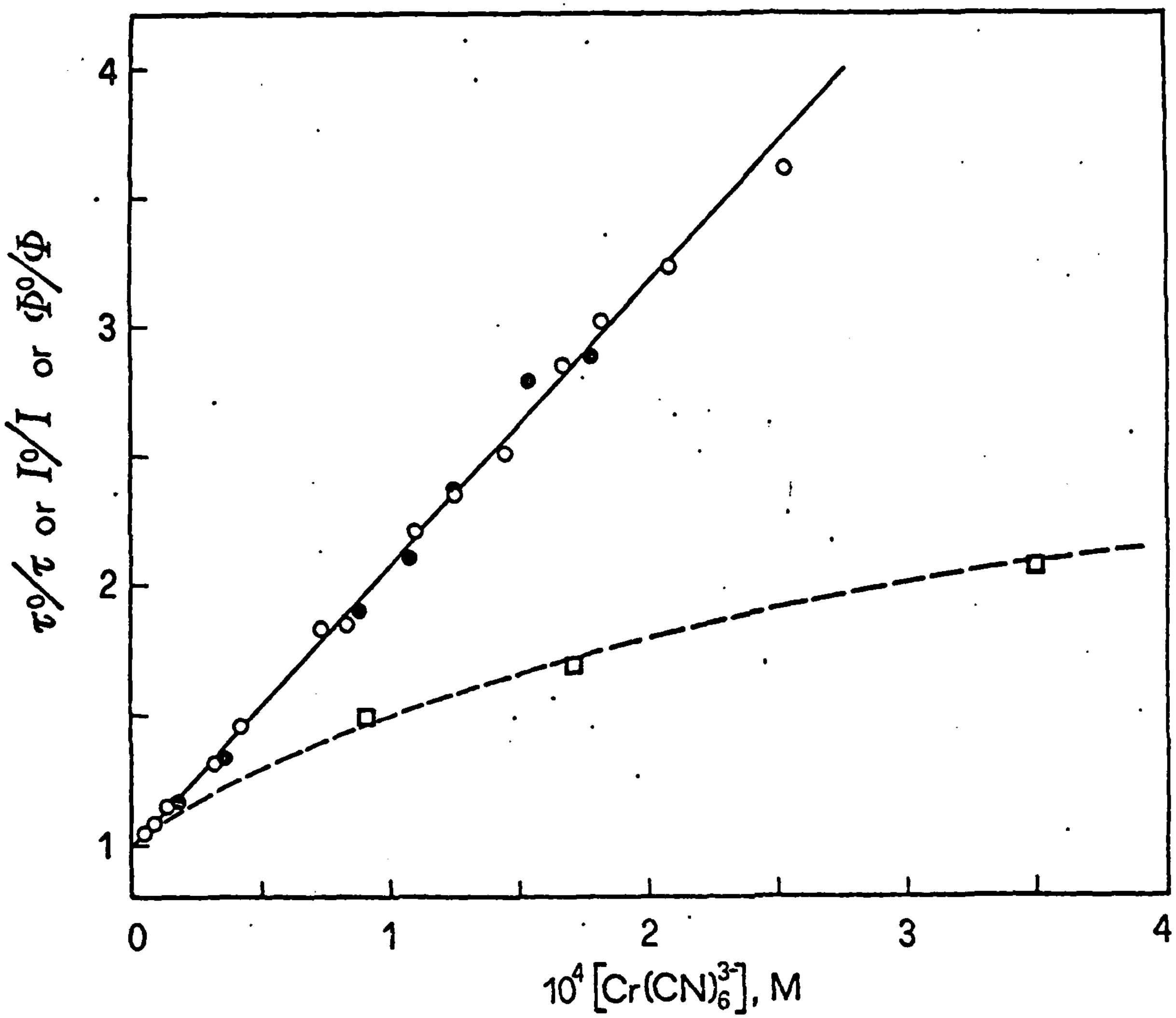
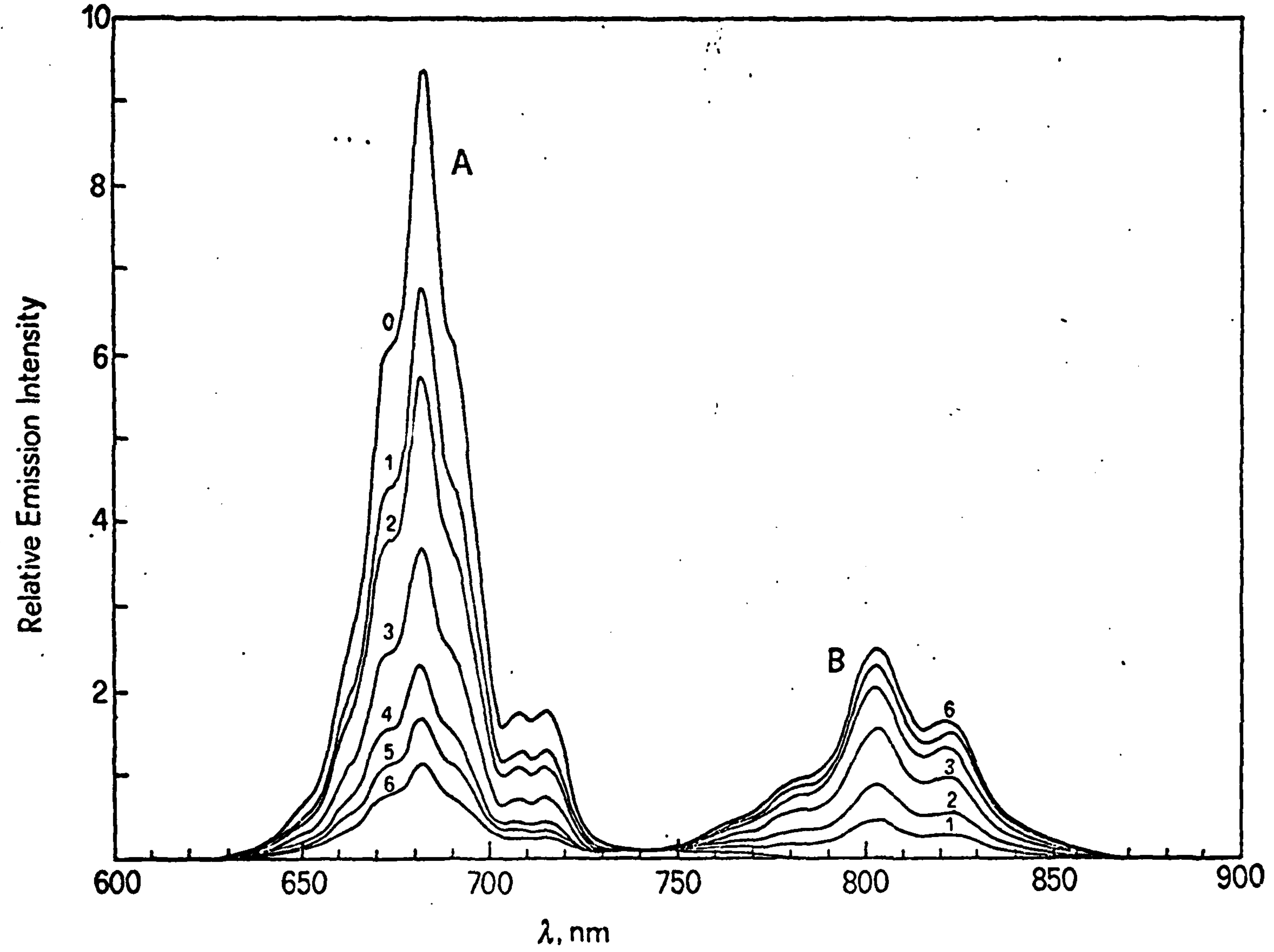


Fig 4

Fig. 3


10
8
6
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Relative Emission Intensity
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1

Fig 4

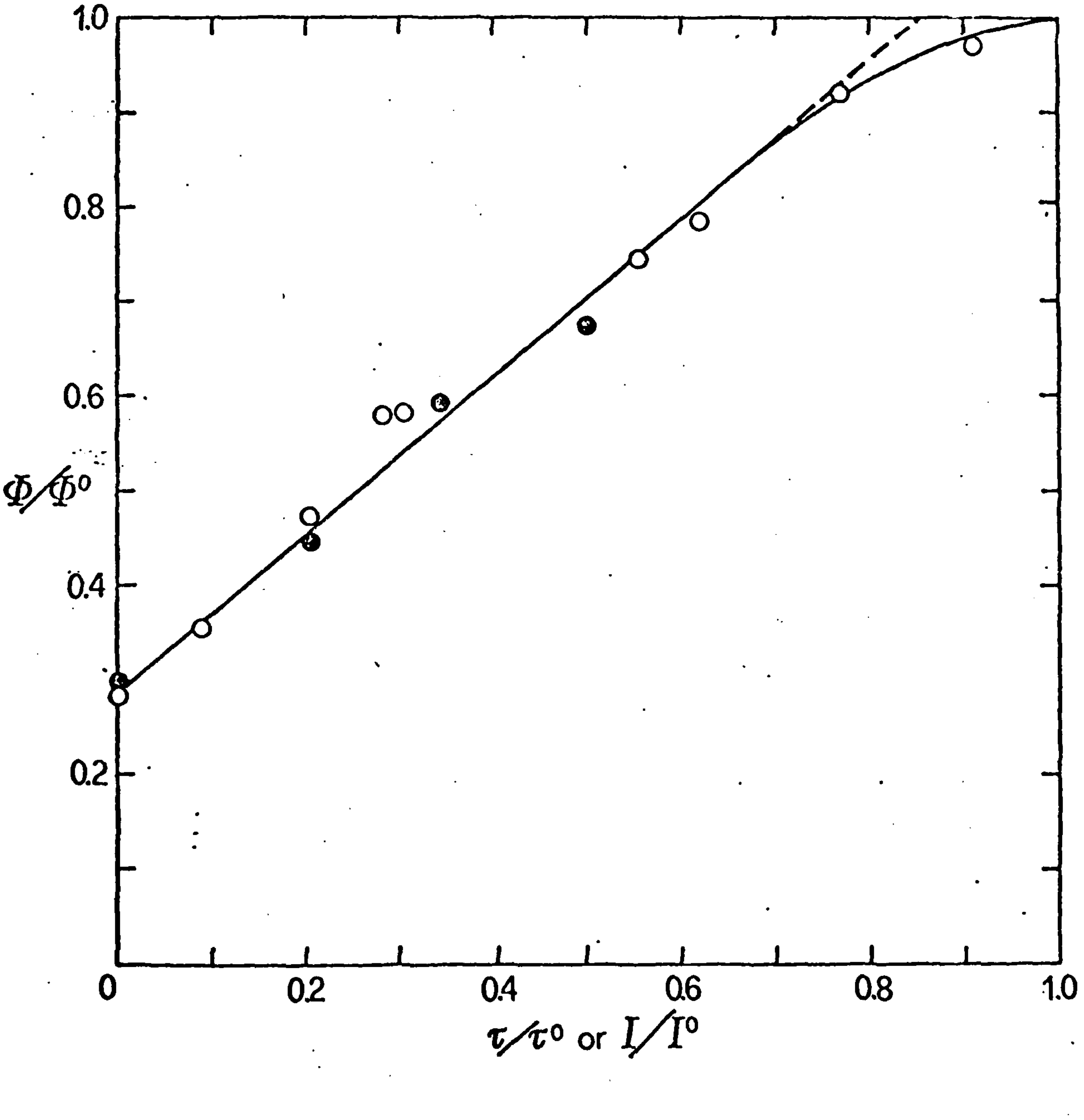

Fig 6

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