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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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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 and 65 μs for pH 3 solutions, respectively, and the corresponding activation energies are 11.2 and 6.6 kcal mol^{-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 6.2×10^8 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 mol^{-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 as follows:

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 pseudooctahedral 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_1^0 to avoid symmetry-specific notations. The superscript zero indicates that the state is thermally equilibrated, or a thexi state. The radiative lifetime of a D_1^0 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 usual assumption that k_r, the radiative rate constant, is essentially temperature independent, then the decrease in emission lifetime, τ, at higher temperatures must be due to the intervention of one or more of the other processes whereby D_1^0 can disappear. These other processes comprise nonradiative relaxation to the ground quartet state, Q_0^0, chemical reaction, and back intersystem crossing to the first excited quartet state, Q_1^0. 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

$$1/\tau = k_{nr} + k_{cr} + k_{bisc} \quad (1)$$

The systems whose behavior originally 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_1^0 states may be chemically reactive (see ref 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 Section

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 sieves and distilled at reduced pressure, under nitrogen atmosphere, before use.

Equipment and Procedures. Emission lifetime measurements were made with the use of essentially the same equipment as that described

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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 $Ru(2,2'\text{-bpy})_3^{2+}$, the yield of the latter being taken as 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 with 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 buffer was used, the concentration of which varied between 5×10^{-3} and 5×10^{-2} M, and was such that the buffer index was the same ($\beta = 5 \times 10^{-3}$) in all cases, allowing a ΔpH of less than 0.05, during photoreaction. Samples of lower and higher pHs were prepared by use of $HClO_4$ or NaOH. Solutions with $Cr(CN)_6^{3-}$ as quencher were also 5×10^{-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 ($HClO_4$) or 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 with use of 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 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 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 acidic 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 pHs in the range 2.7–4.0, the irradiation was interrupted periodically and the pH measured to obtain the amount of ammonia released. In the case of irradiations at natural or basic pHs, an aliquot of standardized perchloric acid solution was added, sufficient to bring an unirradiated solution to pH 3.00. For an irradiated solution, 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.

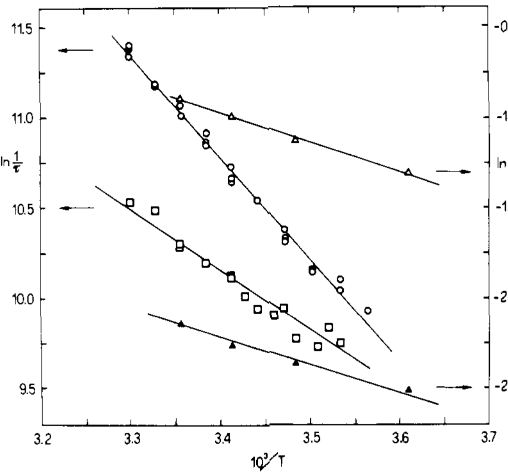

Figure 1. Temperature dependence of emission and photochemistry. Emission lifetimes at pH 5.0: (○) $Cr(NH_3)_5(CN)^{2+}$; (□) *trans*-$Cr(NH_3)_4(CN)_2^+$. Ammonia photoaquation yields for $Cr(NH_3)_5(CN)^{2+}$: (△) pH 3.3; (▲) pH 11.7.

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-gray solid would precipitate out. The spectrohotometric 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 4 × 1 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 product 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 1 h, so as to allow complete conversion of the aquocyano isomers to the corresponding $Cr(NH_3)_4(H_2O)_2^{3+}$ species. The ligand field absorption spectra of these mixtures were then recorded, and the chromium content was determined spectrophotometrically at 374 nm ($\epsilon = 4760$ 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 were 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_1^0 emission from aqueous $Cr(NH_3)_5(CN)^{2+}$ is relatively long, $\tau = 22.4 \pm 0.8$ μs 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 $1/\tau = 1.1 \times 10^{13} \exp(-5650/T)$ s^{-1}, corresponding to an apparent activation energy of 11.2 ± 0.3 kcal mol^{-1}. The emission yield at 20 °C is 0.0020 for 436 ± 3 nm excitation.[23]

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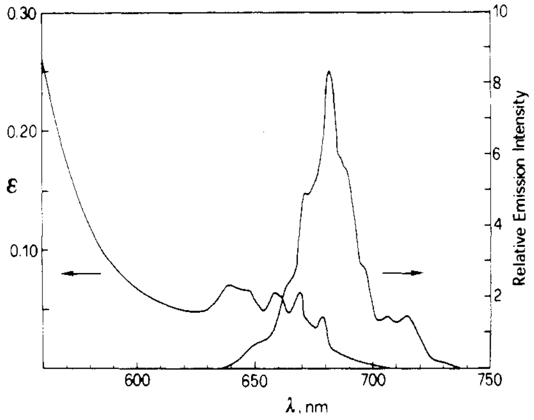

Figure 2. Doublet absorption region (left scale) and emission spectrum (right scale) for $Cr(NH_3)_5(CN)^{2+}$ in acidic aqueous solution.

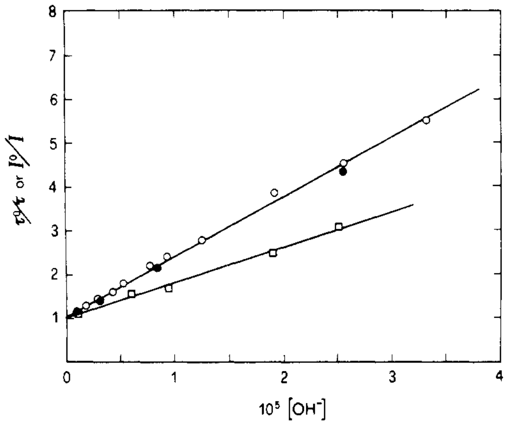

Figure 3. Stern–Volmer type plot for hydroxide quenching of emission at 20 °C for $Cr(NH_3)_5(CN)^{2+}$ (○, τ^0/τ; ●, I^0/I) and *trans*-$Cr(NH_3)_4(CN)_2^+$ (□, τ^0/τ).

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 that 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 $D_1{}^0$ state are involved.

The emission is quenched by hydroxide ion, and the relevant 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 × 10^9 M^{-1} s^{-1}, as defined by the equation

$$I^0/I = \tau^0/\tau = 1 + k_{SV}[Q] \qquad k_{SV} = \tau^0 k_q \qquad (2)$$

Here, I denotes emission yield and the superscript zero denotes values 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 × 10^8 M^{-1} s^{-1} for 20 °C.

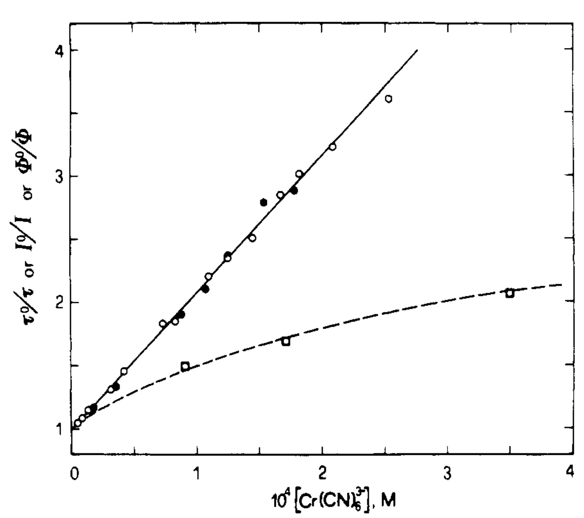

Figure 4. Stern–Volmer type plot of quenching of $Cr(NH_3)_5(CN)^{2+}$ by $Cr(NH)_6{}^{3-}$ in aqueous solutions at pH 3.3 and 20 °C: (○) emission intensity; (●) emission lifetime; (□) ammonia photoaquation yield.

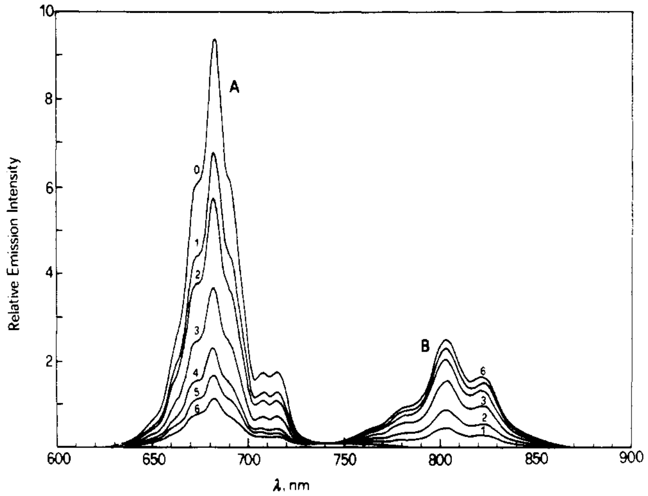

Figure 5. Emission spectra at 20 °C of $Cr(NH_3)_5(CN)^{2+}$ (A) and $Cr(CN)_6{}^{3-}$ (B) upon 470-nm excitation of 5.0 × 10^{-3} M A in DMF, in the presence of increasing concentrations of B. The sequence of concentrations of B (M) is as follows: (0) none; (1) 9.8 × 10^{-6}; (2) 2.0 × 10^{-5}; (3)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

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^0/I and τ^0/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, $k_{SV} \simeq 3 \times 10^4$ M^{-1} at 20 °C. Sensitized emission, of $Cr(CN)_6{}^{3-}$ was also observed following pulse excitation at 530 nm, where only $Cr(NH_3)_5$-

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(23) For a general tabulation of emission yields of Cr(III) complexes, see: Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

(24) The values of [OH^-] are calculated from the pH measurements, with use of K_w = 6.77 × 10^{-15}; they are presumably more nearly OH^- ion activities than concentrations.

(25) Wasgestian, H. F. *J. Phys. Chem.* **1972**, *76*, 1947.

(26) The emission lifetime for the tetrabutylammonium salt of $Cr(CN)_6{}^{3-}$ in degassed DMF solution is 6.0 ms. See: Dannhöl-Fickler, R.; Kelm, H.; Wasgestian, H. F. *J. Lumin.* **1975**, *10*, 103.

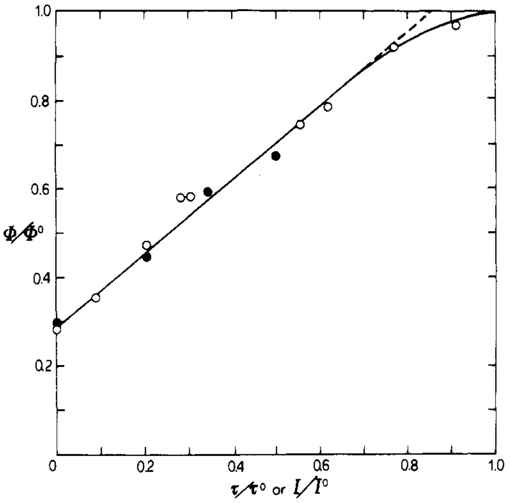

Figure 6. Quenching of ammonia photoaquation of $Cr(NH_3)_5(CN)^{2+}$ vs. emission quenching, under the same conditions. Quenchers are (○) OH^- and (●) $Cr(CN)_6^{3-}$.

$(CN)^{2+}$ absorbs. A 4 × 10^{-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 μs. 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, 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, ϕ_{lim}, of 0.10 ± 0.01 at pHs above 11, that is, under conditions of complete emission quenching. The results are summarized in Table I. For pHs between 8 and 10, the plot of ϕ/ϕ^0 vs. τ/τ^0 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 that 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 τ begins aroung pH 6.5, the decrease in ϕ 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 ϕ values show an apparent activation energy of 3.3 ± 0.3 kcal mol^{-1} under pH 3.3 conditions and one of 3.0 ± 0.3 kcal mol^{-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. The difference, $\phi(\text{pH } 3.3) - \phi(\text{pH } 11.7)$, gives the quenchable yield; its temperature dependence corresponds to an apparent activation average of 3.6 kcal mol^{-1}.

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 $Cr(CN)_6^{3-}$.

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

temp, °C	pH	$[OH^-]$, M	$[Cr(CN)_6^{3-}]$, M	ϕ_{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	2.8 × 10^{-8}		0.370 ± 0.010 (3)
20	6.82	6.0 × 10^{-8}		0.372 ± 0.010 (2)
20	7.35	2.0 × 10^{-7}		0.373 ± 0.010 (3)
20	7.79	5.6 × 10^{-7}		0.358 ± 0.010 (3)
20	8.44	2.5 × 10^{-6}		0.340 ± 0.010 (4)
20	8.79	5.6 × 10^{-6}		0.290 ± 0.010 (4)
20	8.92	7.5 × 10^{-6}		0.276 (1)
20	9.39	2.2 × 10^{-5}		0.216 ± 0.010 (3)
20	9.44	2.5 × 10^{-5}		0.214 (1)
20	9.62	3.8 × 10^{-5}		0.175 (1)
20	10.04	9.9 × 10^{-5}		0.131 ± 0.010 (2)
20	10.67	4.2 × 10^{-4}		0.110 ± 0.010 (2)
20	11.67	4.2 × 10^{-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		9.1 × 10^{-5}	0.250 (1)
20	3.3		1.7 × 10^{-4}	0.219 (1)
20	3.3		3.5 × 10^{-4}	0.179 (1)
20	3.3		2.3 × 10^{-3}	0.114 (1)
20	3.3		8.0 × 10^{-3}	0.111 ± 0.004 (4)

[a] Conditions: irradiation at 465 nm; $\mu = 0.10$; $f_{OH^-} = 0.755$; $K_w = 6.77 \times 10^{-15}$ at 20.0 °C. [b] Number of determinations in parentheses.

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 acidic and basic medium. Photolysis in 1 × 10^{-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.

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 mol^{-1} and a preexponential factor of 1.9 × 10^9 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 3.7 × 10^{-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 above 50% thermal aquation, the fast component, now quite apparent, showed a lifetime of 205 ns, while the lifetime of the slow component had 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 de-

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[28] This value, obtained by seven independent runs, is higher by ca. 10% than the published one, for an ionic strength of 0.5 M.[6] The discrepancy may be partially accounted for by previous experimental difficulties in determining NH_3.

[29] See, for example: Ballardini, R.; Varani, G.; Wasgestian, H. F.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947. Note that the equation ϕ/ϕ^0 = (fraction of unquenchable yield) + (fraction of quenchable yield)τ/τ^0 still applies if some fraction f of quenching encounters are reactive, that is, lead to product formation.

[30] The previously reported value of 34 ± 3% trans isomer agrees within experimental error. Analytical improvements probably make the present result the more accurate one.

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

	quencher	
parameter	OH^-	$Cr(CN)_6{}^{3-}$
k_{SV} from $(\phi^0 - \phi_{lim})/(\phi - \phi_{lim})$, M^{-1}	$(7 \pm 1) \times 10^4$	$(8.3 \pm 0.5) \times 10^3$
k_{SV} from I^0/I, M^{-1}	$(1.2 \pm 0.1) \times 10^5$	$(1.1 \pm 0.1) \times 10^4$
k_{SV} from τ^0/τ, M^{-1}	$(1.3 \pm 0.1) \times 10^5$	$(1.2 \pm 0.1) \times 10^4$
k_q from τ^0/τ, $M^{-1}\ s^{-1}$	$(6.2 \pm 0.3) \times 10^9$	$(6.2 \pm 0.5) \times 10^8$
k_q from I^0/I, $M^{-1}\ s^{-1}$ [a]		1.7×10^9

[a] In DMF solution; data of Figure 5.

crease in value. Thus at 82% aquation, τ for the slow component had dropped to 28 μs. The behavior of this component obeyed the equation $1/\tau = (0.71 \times 10^7)[B] + 1.53 \times 10^4$, with τ in seconds and [B] in molar units. Extrapolation to zero content of the 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 τ 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 0.5×10^{-3} M solution to 56 μs for 3.8×10^{-3} M solution, the progression in τ 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 2.0×10^9 M^{-1} s^{-1} at 20 °C; a plot of $1/\tau$ vs. $[OH^-]$ gives τ^0 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 nd 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 cases of $Cr(NH_3)_6{}^{3+}$,[31] $Cr(en)_3{}^{3+}$ (en = ethylenediamine),[32,33] $Cr(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline),[34] and *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 the 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 $D_1{}^0$ $Cr(CN)_6{}^{3-}$ 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 $D_1{}^0$ 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 pHs, B would be present at least partly in the deprotonated form, *trans*-$Cr(NH_3)_4(OH)(CN)^+$, and we have observed that this species has a short emission lifetime. Mixing of excitation energy transfer lifetimes would then have the effect of reducing the apparent τ for A.

Excited-State Kinetic Scheme. Our simple excited-state scheme for a d^3 system is shown in ref 15. We take $Q_1{}^0$ to be more distorted than $D_1{}^0$ 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 pseudooctahedral symmetry and $Q_1{}^0$ 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 $Q_1{}^0$ or from $D_1{}^0$, and we can write

$$\phi = f_{pisc}\phi_{D_1{}^0} + (1 - f_{pisc})\phi_{Q_1{}^0} \tag{3}$$

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(39) Separate measurements give the emission lifetime of B, *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, as 1.1 μs at 20 °C and pH 3.5. The 205-ns lifetime could still be assigned to B, with lifetime shortening resulting from reversible excitation energy transfer with A. Possibly, however, some anation by the phthalate buffer occurred, and B may partially consist of this species.

where f_{pisc} is the fraction of initially produced Franck–Condon quartet excited states that undergo prompt intersystem crossing to $D_1{}^0$. The quantities $\phi_{D_1{}^0}$ and $\phi_{Q_1{}^0}$ are the yields of product formation from the two states. We neglect, at this level of discussion, any prompt reaction, that is, reaction occurring before thermal equilibration to $Q_1{}^0$ or $D_1{}^0$.

A reasonable interpretation of our quenching results, in the case of $Cr(NH_3)_5(CN)^{2+}$, is that 27% of the photochemistry is due to the second term on the right of eq 3, that is, reaction from directly formed $Q_1{}^0$. The quantity $(1 - f_{\mathrm{pisc}})\phi_{Q_1{}^0}$ is then $0.27 \times 0.37 = 0.10$. The remaining contribution to ϕ, 0.27, is then attributed to molecules undergoing prompt intersystem crossing to $D_1{}^0$. This quenchable portion of the yield may now be assigned either to direct reaction from $D_1{}^0$ or to reaction from $Q_1{}^0$ produced by back intersystem crossing from $D_1{}^0$.

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.

We return, therefore, to the first category of explanation, and it remains to consider whether the actual process is one of direct $D_1{}^0$ reactivity or one of back intersystem crossing followed by $Q_1{}^0$ reaction. A preliminary point is that the emission decay from $D_1{}^0$ is activated by 11.2 and 6.5 kcal mol^{-1} for the mono- and dicyano complexes, respectively. In reference 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 mol^{-1} range. The $D_1{}^0$ 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 $D_1{}^0$ 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 nonbonding 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 that 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 instersystem crossing could show a 6–11 kcal mol^{-1} activation either because this is the $Q_1{}^0$–$D_1{}^0$ energy difference or because of activation energy for a process requiring both a change in molecular geometry and in spin. In the present case, incidently, it is difficult to estimate the $Q_1{}^0$–$D_1{}^0$ energy gap because of the considerable overlap of the vibronic features of the absorption and emission bands.

The observation that the apparent activation energy for emission (11.2 kcal mol^{-1}) is larger than that for the quenchable quantum yield, ϕ_q (3.6 kcal mol^{-1}), does not help as to choice of scheme. ϕ_q depends on the ratio $k_x/(k_r + k_{nr} + k_x)$, where k_x is either k_{cr} or k_{bisc}, while τ^0 depends on the sum $k_r + k_{nr} + k_x$. If, as we suppose, k_x is large compared to k_r and k_{nr}, then the temperature dependence of ϕ_q will not depend on that of k_x, but the temperature dependence of τ^0 will; this will be true regardless of whether $k_x = k_{cr}$ or $k_x = k_{\mathrm{bisc}}$.

The fact that the photoreaction made 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 $Q_1{}^0$ were important.[6,7] The observation that the temperature dependence of ϕ is about the same for both the quenchable and the unquenchable portion, in the case of $Cr(NH_3)_5(CN)^{2+}$, and is smaller than for τ, namely 3 vs. 11 kcal mol^{-1}, is suggestive although not diagnostic. One explanation is that f_{pisc} has little temperature dependence, essentially all of $D_1{}^0$ back intersystem crosses to Q_1,[41] and $\phi_{Q_1{}^0}$ has a 3 kcal mol^{-1} temperature dependence. In the other scenario, all quenchable reaction is from $D_1{}^0$, and $\phi_{D_1{}^0}$ is now unity.[41] The temperature dependence of the quenchable ϕ would now be assigned to f_{pisc}, and for the unquenchable yield to still have a temperature dependence of 3 kcal mol^{-1} (and not -3 kcal mol^{-1}), the apparent activation energy for $phi_{Q_1{}^0}$ would have to be 6 kcal mol^{-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 $Q_1{}^0$, or that the mechanisms of $D_1{}^0$ and $Q_1{}^0$ 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 $(\phi^0 - \phi_{\mathrm{lim}})/(\phi - \phi_{\mathrm{lim}})$ 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 ϕ/ϕ^0 vs. τ/τ^0 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 an 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]

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(41) Were this not so, then k_{nr} would have to be a competitive exiting process for $D_1{}^0$ (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 mol^{-1} temperature dependence for emission, contrary to observation; also the 11 kcal mol^{-1} apparent activation energy for emission would have to be assigned to k_{nr}, which seems unreasonable. In the alternative scenario, similar difficulties arise if k_{cr} is not dominant, that is, if $\phi_{D_1{}^0}$ is not essentially unity.

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

(43) Huchital, D.; Adamson, A. W., unpublished work.

Summary

We may summarize as follows. The emission rules cited in the Introduction correctly predict that the emission lifetimes for aqueous $Cr(NH_3)_5(CN)^{2+}$ and *trans*-$Cr(NH_3)_4(CN)_2^+$ are relatively long. Both complexes show emission quenching by OH^-, and for the former, quenching by $Cr(CN)_6^{3-}$ was also studied (both in aqueous and in DMF solution). There are detailed temperature dependence data.

There were complexities in the case of the dicyano complex, stemming from interaction with the aquocyano thermal aquation product, probably excitation energy transfer. Biphasic emission decay was observed to progress in importance with the degree of thermal aquation.

In the case of $Cr(NH_3)_5(CN)^{2+}$, the quantum yield for aquation of ammonia (the observed mode of photoreaction) also shows both OH^- and $Cr(CN)_6^{3-}$ quenching, but with 27% of unquenchable yield. The photolysis produces both *trans*- and *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, and the product isomer ratio is essentially the same for the quenchable and the unquenchable fractions of reaction. Again, there are temperature dependnece studies.

It seems likely that, following excitation, some prompt intersystem crossing occurs, so that both the thexi states D_1^0 and Q_1^0 are formed promptly. Neither the quenching behavior nor the temperature dependencies are diagnostic as to whether the quenchable portion of the photoreaction is due to direct reaction from D_1^0 or to reaction from Q_1^0 formed by back intersystem crossing. The invariance of the isomer ratio suggests the latter situation, however.

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Registry No. $Cr(NH_3)_5(CN)^{2+}$, 42213-67-2; *trans*-$Cr(NH_3)_4(CN)_2^+$, 76299-50-8; $Cr(CN)_6^{3-}$, 14875-14-0; *cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, 74482-64-7; *trans*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$, 74523-68-5; OH^-, 14280-30-9.

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Nature of the Residual Paramagnetic Fraction in Discontinuous and Continuous High-Spin (${}^5T_2$) $\rightleftharpoons$ Low-Spin (${}^1A_1$) Transitions of Iron(II) Complexes

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Detailed investigations of the ^{57}Fe Mössbauer-effect parameters and X-ray powder diffraction have been performed for the iron(II) complexes $[Fe(phy)_2](ClO_4)_2$ and $[Fe(bts)_2(NCS)_2]$ as a function of temperature (phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone; bts = 2,2′-bi(5-methyl-2-thiazoline)). The high-spin (${}^5T_2$) $\rightleftharpoons$ low-spin (${}^1A_1$) transition in $[Fe(phy)_2](ClO_4)_2$ is of the discontinuous type ($T_c \simeq$ 247–252 K); that in $[Fe(bts)_2(NCS)_2]$ is of the continuous type ($T_c \simeq$ 219.5 K). For both compounds, the quadrupole splitting $\Delta E_Q({}^5T_2)$ shows a pronounced discontinuity in the region of T_c. The discontinuity arises since the ΔE_Q values for the residual paramagnetic molecules are different from those of the bulk paramagnetic phase above T_c. It is proposed that, for the discontinuous spin transitions, the small crystallites that cannot participate in the crystallographic phase change are responsible for the residual paramagnetism at low temperatures. For the majority of the continuous transitions, the residual paramagnetic fraction is formed by those molecules that are trapped at defect sites within the lattice of the bulk low-spin isomer. The conclusions are supported by the results of grinding experiments as well as by the results for various additional crossover compounds.

Introduction

In a number of investigations[2–4] of various iron(II) complexes it has been observed that the high-spin (${}^5T_2$) $\rightleftharpoons$ low-spin (${}^1A_1$) transition is not completed at the two extreme temperatures and that there exists a certain fraction of molecules that do not participate in the transition. These molecules have been termed, in particular at the low-temperature extreme of the measurements, the residual paramagnetic fraction, their magnitude being strongly dependent on the method of preparation and the physical status of the sample. Although it is possible to establish reliably the existence of this type of molecule, e.g. from magnetic susceptibility studies, thus far only speculations concerning its origin and characterization have been published. The application of ^{57}Fe Mössbauer spectroscopy should assist in the determination of the nature of these molecules, since it is a microscopic technique. In particular, it may be of interest to compare the temperature dependence of the Mössbauer parameters for the residual fraction with that for the bulk paramagnetic phase above the transition temperature. Whereas for the high-spin (${}^5T_2$) state of iron(II) the value of the quadrupole splitting is rather sensitive to lattice distortions,[5] for the low-spin (${}^1A_1$) state this is not the case. Consequently, it may be expected that at least for the high-spin (${}^5T_2$) state it should be possible to distinguish the residual paramagnetic fraction from the main part of the high-spin phase of the substance.

Indeed, a clear discontinuity in the values of the quadrupole splitting $\Delta E_Q({}^5T_2)$ has been reported in the spin-transition region for *precipitated* samples of $[Fe(phen)_2(NCS)_2]$ by Ganguli et al.[6] (phen = 1,10-phenanthroline). The observed discontinuity has been attributed to a crystallographic phase change that is believed to be associated with the high-spin (${}^5T_2$) $\rightleftharpoons$ low-spin (${}^1A_1$) transition in the compound. However, subsequent studies[7] of the Mn^{2+} ion EPR on samples of $[Fe(phen)_2(NCS)_2]$ doped with 1 mol % Mn^{2+} did not reveal any indication for the proposed crystallographic phase change.

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