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Solution phosphorescence of *trans*-cyanoacidotetraammine-chromium(III) complexes. Comparison with models for doublet-state deactivation

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Abstract

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ ions, where X denotes CN^-, NH_3, NCS^-, H_2O, F^- and Cl^-, exhibit fairly intense and long-lived emissions compared with those of analogous species not containing cyanide ligands. The phosphorescence decay rates in acidic aqueous solution around room temperature, and their activation parameters, are examined for the whole series. The lifetime values at 20 °C vary between 40 and 0.26 μs, and obey Adamson's empirical emission rules. The activation energies are in the 25-55 kJ mol^{-1} range. The data are discussed in terms of the possible processes controlling the doublet-state lifetime under ambient conditions.

1. INTRODUCTION

The involvement of the lowest excited doublet state in the photochemical reactivity of chromium(III) complexes has long been a point of major interest [1-5]. The recognition that such a state often emits detectable phosphorescence in ambient-temperature fluid solution has provided a valuable tool for addressing the question mainly by two kinds of procedures: (i) comparison of emission and photoreaction quenching under identical conditions and (ii) study of ligand, structural and environmental effects on the phosphorescence lifetimes and on their temperature dependence.

As a result of the former investigations the unquenchable photochemistry upon complete doublet quenching has unanimously been attributed to the short-lived, lowest excited quartet state formed in competition with prompt intersystem crossing to the longer-lived doublet during vibrational relaxation of Frank-Condon states. In regard to the quenchable, doublet-mediated reactivity, it has been customary to explore three possibilities: (a) back intersystem crossing followed by quartet reaction, (b) direct doublet reaction and (c) crossing to a reactive ground-state intermediate. There is evidence that no uniform mechanism applies to all chromium(III) species, and indications as to which process is prevailing in a given system are sought through the second type of experiments, specially in relation to the thermal activation expected for each of these pathways. For such an approach, series of closely related complexes are, of course, desirable, enabling systematic variations of single factors such as, for example, one of the ligands, the geometric isomerism, the degree of steric restriction, and so forth.

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Table 1
Photophysical parameters and ligand-field photoaquation behavior of *trans*-$Cr(NH_3)_4X(CN)^{z+}$ complexes in acid aqueous solution

X	τ_{20} µs	E^* kJ mol^{-1}	ln A	$\delta E(^4E\text{-}^4B_2)$ cm^{-1}	Photolyzed ligands
CN^- [a]	40	27.5	21.4	2520	$NH_3 \gg CN^-$ [c]
NH_3 [a]	22	47.0	30.0	1260	$NH_3 \gg CN^-$ [d]
NCS^- [b]	30	38.1	26.1	300	$NH_3 > CN^- > NCS^-$ [e]
H_2O [b]	1.10	54.9	36.3	-170	$H_2O > CN^- \sim NH_3$ [e]
F^-	0.26	46.8	34.4	-280	$NH_3 > CN^- > F^-$ [e]
Cl^-	0.26	45.5	33.8	-860	$CN^- > NH_3 \gg Cl^-$ [f]

[a] Emission data from [16]. [b] Emission data from [14]. [c] [12]. [d] [11]. [e] [14]. [f] [15].

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ compounds with X = CN^-, NH_3, H_2O, NCS^-, F^- and Cl^-, synthesized [6-9] and characterized both thermally [6,9,10] and photochemically [11-15] in this laboratory over the past decade, form a particularly homogeneous and fairly wide-ranging group of good chromium(III) emitters. Their phosphorescence lifetimes in solution are, in fact, at least two orders of magnitude longer than those of the analogous *trans*-$Cr(NH_3)_4XY^{z+}$ or *trans*-$Cr(en)_2XY^{z+}$ ions with $Y \neq CN^-$ [5], so that rate and activation parameters for the decay of the emitting state are measurable with accuracy. This report combines previous separate results [14,16] as well as new data on the photophysics of these complexes in aqueous medium, in order to compare the behavior of the whole family with the models proposed for doublet-state deactivation of chromium(III).

2. EXPERIMENTAL

The *trans*-$Cr(NH_3)_4X(CN)^{z+}$ complexes, where X stands for NH_3 [6], CN^- [7,8], H_2O [8], NCS^-, F^- and Cl^- [9], were prepared by published methods, as the perchlorate salts. The apparatus and procedures for measuring absorption and emission spectra and for determining the phosphorescence decay rates have been described elsewhere [14,16]. Excitation in the ligand-field absorption region was by means of 20-ns pulses from either a frequency-tripled Nd laser (353 nm) or a frequency-doubled ruby laser (347 nm). Samples were $(1.0\text{-}2.0) \times 10^{-2}$ M in complex and 1×10^{-3} M in $HClO_4$, and were filtered through 0.45-µm Millipore cellulose filters. The temperature was controlled within 0.2 °C. Lifetime values were obtained from least-squares fittings of the first-order decay plots, with correlation coefficients larger than 0.998 and reproducibilities within 5%.

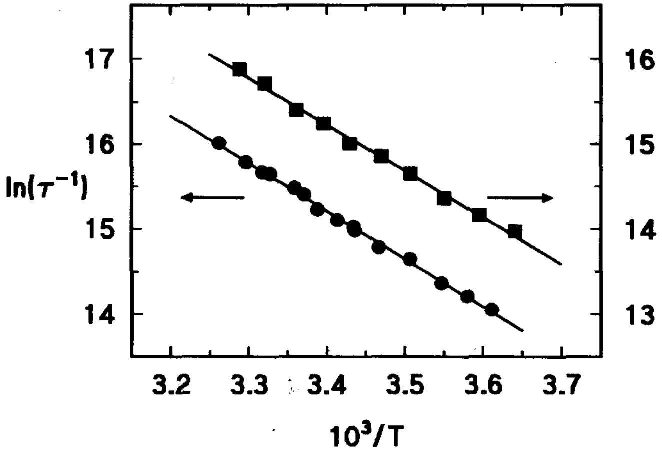

Figure 1. Temperature dependence of the emission lifetimes of *trans*-$Cr(NH_3)_4X(CN)^+$ ions in 1 × 10^{-3} M $HClO_4$ solution: (■) X = Cl^- (right scale); (●) X = F^- (left scale).

3. RESULTS

The phosphorescence lifetimes at 20 °C, τ_{20}, and their activation parameters are collected in Table 1, where the six complexes are arranged according to decreasing field-strength of the X ligand. New results are those relative to the species with X = F^- and Cl^-. Ten to twenty emission decay rates were generally measured for each compound over 20-30 °C temperature intervals between 0 and 35 °C. The decays were mono-exponential in all cases. For the systems having the longer-lived emissions, some lifetime variations were noticed, arising either from changes of the complex concentration or from the quenching by thermal and photochemical aquation products. Care was taken to minimize these effects.

The temperature dependence for X = F^- and Cl^- is illustrated in Figure 1. Analogous plots for the other complexes have already been reported [14,16]. The apparent activation energies, E^*, and frequency factors, A, were obtained by fitting the data to the equation $\tau^{-1} = A \exp(-E^*/RT)$. Least-squares correlation coefficients were always greater than 0.995 and standard deviations less than ±3%.

Table 1 includes the first-order energy separations, δE, between the ^4E and $^4B_2$ excited states of octahedral $^4T_{2g}$ parentage, which are directly related to the spectrochemical position of X. Such splittings are evaluated by means of the angular overlap model relationship $3/2(\sigma_{ax} - \sigma_{eq}) - 2(\pi_{ax} - \pi_{eq})$, as a function of the axial and equatorial averages of the σ_L and π_L ligand parameters available from the literature [4]. The last column of the Table summarizes the photochemistry of the complexes by reporting the order of leaving ability of the various ligands upon excitation in the ligand-field region [11-15].

Figure 2 displays the Arrhenius parameters in a Barclay-Butler plot. The line represents the best fit previously reported for a dozen complex-solvent combinations involving

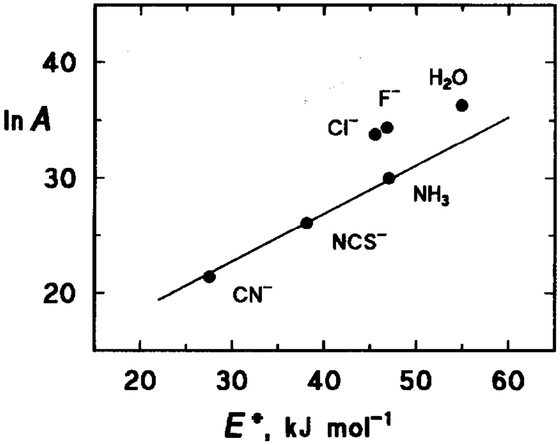

Figure 2. Barclay-Butler plot of the Arrhenius parameters for emission decay of *trans*-$Cr(NH_3)_4X(CN)^{z+}$ complexes in aqueous solution. The line is from [16].

$Cr(NH_3)_5(CN)^{2+}$ and the two $Cr(NH_3)_4(CN)_2{}^+$ isomers [16], and is given by eqn. (1)

$$\ln A = 10.2 + 0.418E^* \qquad (1)$$

The ligand-field absorption and emission maxima in aqueous solution (pH 3, $HClO_4$) are listed in Table 2. The anticipated splittings of the low-energy quartet absorption bands are in no case apparent due to the relatively small $\delta E(^4E\text{-}^4B_2)$ values (Table 1). The first excited quartet state and the associated maximum are designated by the general notation Q_1. The energy of the thermally equilibrated excited quartet, $Q_1{}^0$, is estimated from the empirical equation $E(Q_1{}^0) = 1.11\nu_{0.05} - 0.88$, where $\nu_{0.05}$ (in 10^3 cm^{-1} units) denotes the position at which the absorption intensity is 5% of that of the band maximum [17]. The corresponding wavelengths are indicated in the Table as $\lambda(Q_1)_{0.05}$. The phosphorescence spectra are narrow and structured [13,14,16]: as usual, the prominent peaks are taken to measure the energy of the zero vibrational level of the lowest doublet state, labeled $D_1{}^0$.

4. DISCUSSION

Table 1 shows that within the *trans*-$Cr(NH_3)_4X(CN)^{z+}$ series the doublet-state solution lifetimes vary over more than a 100-fold range, and suggests a first empirical comparison with the emission rules formulated by Adamson [18]. The rule applicable to mixed-ligand systems is that, when the complex is treated as pseudooctahedral, *the emission lifetime in room-temperature fluid solution will be relatively short (< 1 μs) if that ligand which is preferentially substituted in the thermal reaction lies on the weak-field axis.*

This prediction is well obeyed here. For all complexes the ground-state reactivity

Table 2
Spectral data for *trans*-$Cr(NH_3)_4X(CN)^{z+}$ complexes and related quantities

X	$\lambda(Q_1)^a$ nm	$\lambda(Q_1)_{0.05}^b$ nm	$\lambda(D_1^0)^c$ nm	$E(Q_1^0)^d$ cm^{-1}	ΔE_{QD}^e cm^{-1}	E^{*f} cm^{-1}
CN^-	440	526	700	20 220	5930	2290
NH_3	451	528	680	20 140	5430	3930
NCS^-	466	541	709	19 630	5530	3180
H_2O	468	542	688	19 600	5070	4590
F^-	483	568	685	18 680	4080	3910
Cl^-	488	574	697	18 480	4130	3800

[a] Absorption maxima. [b] See text. [c] Emissin maxima. [d] 5% absorption rule [17].
[e] Calculated Q_1^0-D_1^0 energy separations. [f] Experimental activation energies.

consists of acid-catalyzed aquation of cyanide [6,9,10]; in the X = Cl^- case this competes with pH-independent loss of chloride [9]. The thermally labile groups thus define the tetragonal axis. On going from X = CN^- to X = Cl^- the average ligand-field strength along such an axis changes regularly from higher to lower values with respect to the field strength of the equatorial plane. This is better evidenced by the variation of $\delta E(^4E\text{-}^4B_2)$ (Table 1), which depends on the difference between axial and equatorial fields [4]. For X = NCS^-, H_2O, F^- and Cl^-, the cyano and X ligands act in opposition on the $^4T_{2g}$ splitting, so that from an electronic point of view there is little departure from O_h symmetry, while the molecular geometries remain truly tetragonal.

The complexes with the longer-lived phosphorescence are indeed those where the weak-field axes are the NH_3-NH_3 ones and do not contain the thermally released ligands. The shorter emission lifetimes are then observed when the weak-field axis is the X-CN^- one. It may be noticed that the intermediate τ_{20} value of ca. 1 μs pertains to the X = H_2O species which is the closest to the O_h situation. As was pointed out earlier [16], any attempt to go beyond a rough correlation between the order of magnitude of the lifetime and the spectrochemical position of X would be meaningless: severalfold changes in τ may arise from balancing of as much as 10^6-fold variations of the frequency factor A and nearly matching opposite variations of $\exp(E^*/RT)$ in the Arrhenius equation.

Considering the pathway through which the emitting state actually disappears, as already mentioned, the three potential contributions under the present conditions are back intersystem crossing (BISC), chemical reaction (CR) and surface crossing to an intermediate in its ground electronic state (GSI): in principle,

$$\tau^{-1} = k_{BISC} + k_{CR} + k_{GSI} \qquad (2)$$

The relative importance of these processes for chromium(III) systems continues to draw much attention [5,19-24], and we examine here what may be inferred from our data.

The emission rules were rationalized in terms of chemical control (k_{CR}) of the doublet lifetime [18]. It was proposed that if the dominant photolysis mode is the same as the thermal mode, it would be facilitated by a similar substitution mechanism because of the electronic and geometric similarities of the doublet and the ground state, and k_{CR} would be large. Antithermal photoreactions would consequently be associated with smaller k_{CR} values. The photochemistry of the *trans*-$Cr(NH_3)_4X(CN)^{z+}$ family is fairly consistent with this interpretation. As summarized in Table 1, the ligand preferentially photoaquated is, in fact, ammonia when X = CN^- [12], NH_3 [11] and NCS^- [14], and one of the acido groups when X = H_2O [14] and Cl^- [15]. Although in the X = F^- case the prevalent mode is ammonia solvation rather than acido-group solvation, the latter still represents a substantial part of the photoreactivity [14]: this possible exception may be accommodated by the anomalous photobehavior of fluoro-am(m)ine complexes with respect to simple ligand-field predictions [3,4].

Since all the above processes require molecular rearrangements, they are envisaged as thermally activated. The temperature dependence of the emission decay is, therefore, expected to give further indications as to the choice between BISC and the other two possibilities.

It is generally accepted that if k_{BISC} is the limiting term in eqn. (2), the activation energy should somehow parallel the separation, ΔE_{QD}, between the thermally equilibrated excited quartet (Q_1^0) and doublet (D_1^0) states (Table 2). The indirect evaluation of this gap from the spectra is subject to uncertainty arising from the different equilibrium geometries of Q_1^0 and D_1^0; furthermore, the experimental E^* values for BISC are likely to include nonnegligible contributions by other factors such as, for example, solvent reorganization accompanying conversion between these structurally different states. However, within a group of very similar complexes these perturbations should be systematic and some regularity should survive.

If regarded as a single set, the data of Table 2 show no correlation of this kind. The lowest activation energy is exhibited by *trans*-$Cr(NH_3)_4(CN)_2^+$, where the Q_1^0-D_1^0 gap is undoubtedly the largest due to the combined spectrochemical and nephelauxetic effects of two CN^- ligands, which respectively raise the former energy level and depress the latter. If there is any trend along the series, it is opposite to the BISC expectation. Medium effects on the compounds with X = CN^- and NH_3 as well as on the *cis*-$Cr(NH_3)_4(CN)_2^+$ isomer [16] substantiate the improbability of BISC, at least for these species. For a given complex in different solvents E^* can vary up to 100% (or by more than 25 kJ mol^{-1}), whereas very small absorption and emission spectral changes suggest a virtually constant Q_1^0-D_1^0 separation. A photophysical study of several systems ranging from CrO_6 to CrN_6 coordination led to the conclusion that BISC is significant when such a separation is less than 35-40 kJ mol^{-1} [19]. In all the complexes considered here the calculated quartet-doublet spacings are well above this threshold.

While the presumed lack of BISC and the possible correlation of thermal lability with the emission lifetimes are consistent with chemical deactivation of the doublet, the fact that the present complexes contain simple monodentate ligands excludes the steric restriction effects that are investigated to test the GSI alternative [20,23,24]. The data are, therefore, insufficient to distinguish between the CR and GSI routes. In the former case E^* would represent the activation energy for reaction occurring directly from D_1^0, and in the latter the barrier of the vibrationally promoted crossing to the distorted ground-state intermediate from which branching would occur to either the products or the original undistorted complex. The previously noted tendency of the activation energy to increase with the viscosity of the medium is also compatible with both models: remarkable is the doubling of E^* for *trans*-$Cr(NH_3)_4(CN)_2^+$ on passing from water to dimethyl sulfoxide [16].

To the extent that the Barclay-Butler analysis of the activation parameters is diagnostic toward the occurrence of one or more doublet decay processes, Figure 2 provides some additional clues. The data appear to group into two classes, implying two different pathways. The species having the longer-lived emissions fit precisely eqn. (1) which describes the behavior of a number of complex-solvent systems with τ between 10 and 100 µs [16]. The parameters for the short-lived emissions fall outside this plot and, possibly, define another line. A two-pathway description may still be reconciled with the CR hypothesis by assuming two different mechanisms, i.e., two different transition states, for the thermal and the antithermal photoreactions.

As an alternative interpretation, the shorter lifetimes can be ascribed to intervention of BISC, that is, the six compounds would form into two distinct groups associated with CR/GSI and BISC, respectively. Various observations are congruent with this view. (i) For the short-lived emissions E^* and ΔE_{QD} are comparable and indeed appear to correlate, although for a limited set of three data points the correlation may be fortuitous. (ii) For the three other systems the two quantities are unrelated as noted before; moreover, the E^* values are definitely smaller than the ΔE_{QD} ones. (iii) In an exclusive CR context it would be reasonable to expect lower activation energies for the facilitated thermal-type doublet photoreactions than for the antithermal ones, which is contrary to the finding. A possible difficulty with this picture is that the surmountable barrier to BISC would be raised to ca. 60 kJ mol^{-1}, a rather high value according to current thinking; in addition, an abrupt change from one decay mode to another would take place on passing from X = NCS^- to X = H_2O despite a relatively small change (ca. 5 kJ mol^{-1}) in ΔE_{QD}.

To complete the survey of the existing data, independent quenching results for two of the long-lived species suggest a pattern at least in partial disagreement with the above inferences. The quenchable photoreactivities of $Cr(NH_3)_5(CN)^{2+}$ and *trans*-$Cr(NH_3)_4(NCS)(CN)^+$ occurring via D_1^0, have been found to be the same as the unquenchable ones which originate from Q_1^0. In particular, the former complex yields the same *trans-/cis*-$Cr(NH_3)_4(H_2O)(CN)^{2+}$ ratio [13], and the latter the same proportion of photoreleased NH_3, NCS^- and CN^- [14]. This points to a unique precursor to all photochemistry, to say the least. Both the competitive bond labilization and the photostereochemistry are entirely explainable by the quartet-related models [1,3,4], and it is higly improbable that the same photobehavior be exhibited by Q_1^0 and D_1^0 (or an intermediate derived from the latter state), which are characterized by different electron distributions and conceivably different geometries. Thus, on the basis of the chemical evidence BISC appears to be the dominant process along the whole series. This conclusion is not unreasonable in the light of the recently advanced notion that in photoreactive systems the barrier to BISC may be lowered significantly with respect to the spectroscopic value by a strong interaction of the quartet excited state with the nucleophilic solvent, which would distort the potential surface of Q_1 along a coordinate for chemical reaction [25].

To sum up, the data examined here are compatible with more than one interpretation, and the apparent inconsistencies show the lack of a model that accounts for all observations. Uncertainty remains because the intimate mechanism of each of the postulated processes is not yet known.

5. REFERENCES

1 E. Zinato, in A.W. Adamson and P.D. Fleischauer (eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, Chap. 4.
2 M.A. Jamieson, N. Serpone and M.Z. Hoffman, Coord. Chem. Rev., 39 (1981) 121.
3 A.D. Kirk, Coord. Chem. Rev., 39 (1981) 225.
4 L.G. Vanquickenborne and A. Ceulemans, Coord. Chem. Rev., 48 (1983) 157.
5 J.F. Endicott, T. Ramasami, L. Tamilarasan, R.B. Lessard, C.K. Ryu and G.R. Brubaker, Coord. Chem. Rev., 77 (1987) 1.
6 P. Riccieri and E. Zinato, Inorg. Chem., 19 (1980) 853.
7 P. Riccieri and E. Zinato, Inorg. Chem., 20 (1981) 3722.
8 P. Riccieri and E. Zinato, Inorg. Chim. Acta, 177 (1990) 147.
9 P. Riccieri and E. Zinato, Polyhedron, 11 (1992) 71.
10 P. Riccieri and E. Zinato, Inorg. Chem., 24 (1985) 441.
11 P. Riccieri and E. Zinato, Inorg. Chem., 19 (1980) 3279.
12 E. Zinato, P. Riccieri and M. Prelati, Inorg. Chem., 20 (1981) 1432.
13 E. Zinato, A.W. Adamson, J.L. Reed, J.P. Puaux and P. Riccieri, Inorg. Chem., 23 (1984) 1138.
14 P. Riccieri, E. Zinato and A. Damiani, Inorg. Chem., 26 (1987) 2667.
15 P. Riccieri, E. Zinato and A. Damiani, Inorg. Chem., 27 (1988) 3755.
16 E. Zinato, A.W. Adamson and P. Riccieri, J. Phys. Chem., 89 (1985) 839.
17 P.D. Fleischauer, A.W. Adamson and G. Sartori, Prog. Inorg. Chem., 17 (1972) 1.
18 R.T. Walters and A.W. Adamson, Acta Chem. Scand., A33 (1979) 53.
19 G.E. Rojas and D. Magde, Inorg. Chem., 26 (1987) 2334.
20 R.B. Lessard, J.F. Endicott, M.W. Perkovic and L.A. Ochrymowycz, Inorg. Chem., 28 (1989) 2574.
21 L.S. Forster, D. Murrow and A.F. Fucaloro, Inorg. Chem., 29 (1990) 3706.
22 D.A. Friesen, S.H. Lee, J. Lilie, W.L. Waltz and L. Vincze, Inorg. Chem., 30 (1991) 1975.
23 M.W. Perkovic, M.J. Heeg and J.F. Endicott, Inorg. Chem., 30 (1991) 3140.
24 R.B. Lessard, M.J. Heeg, T. Buranda, M.W. Perkovic, C.L. Schwarz, Y. Rudong and J.F. Endicott, Inorg. Chem., 31 (1992) 3091.
25 A.D. Kirk and H.U.Güdel, Inorg. Chem., 31 (1992) 4564.