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Communications

Excited-State Interaction of $Cu(CN)_2^-$ with Halide Ions. Does the Emission Originate from a Simple Inorganic Exciplex?

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Coordinatively unsaturated $^*Cu(CN)_2^-$ formed upon UV irradiation in aqueous solutions of dicyanocuprate(I) associates with halide ions to create longer-lived, more highly luminescent species. The enhancement of the emission and the characteristic change in luminescence lifetime with increasing halide ion concentration is reminiscent of the nature of systems in which exciplexes or excimers form. However, in this system, there is also association in the ground state, which has about an order of magnitude smaller stepwise formation constant than the excited-state reaction. Hence the luminescence characteristics can be explained by a mechanism involving both ground- and excited-state equilibrium reactions. The various rate constants of this mechanism have been determined, indicating that the key reaction is the coordination of the ground-state halide ion to the excited copper(I) complex, resulting in an inorganic luminescent exciplex. Although exciplexes are well-known molecular entities in the photochemistry and photophysics of organic systems, there have been only a few reports of exciplex formation in the inorganic literature.[1-6] Because of the 10-fold higher association of the halo ligand with the excited dicyanocuprate(I) complex compared to the ground-state association, we believe we are justified in calling the emitting species an exciplex.

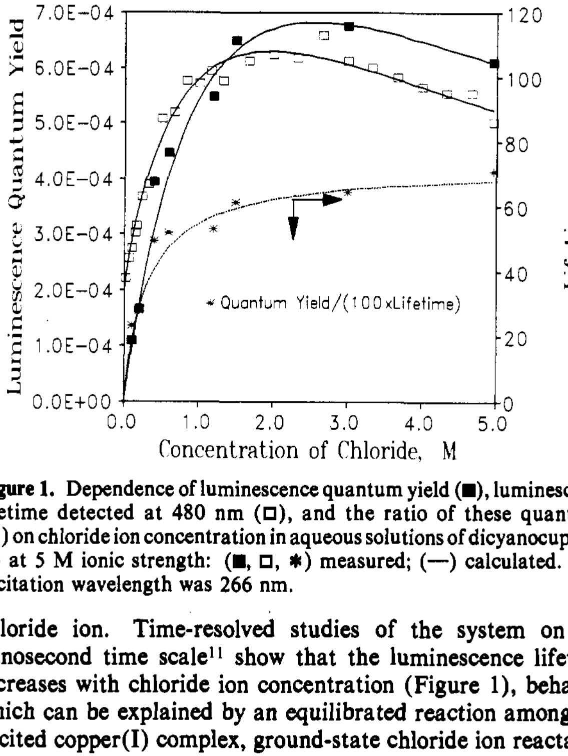

Figure 1. Dependence of luminescence quantum yield (■), luminescence lifetime detected at 480 nm (□), and the ratio of these quantities (✱) on chloride ion concentration in aqueous solutions of dicyanocuprate(I) at 5 M ionic strength: (■, □, ✱) measured; (—) calculated. The excitation wavelength was 266 nm.

We have demonstrated previously[7] that the characteristic luminescence of $Cu(CN)_2^-$ in aqueous solution disappears while a new broad, structureless emission band develops at 480 nm when chloride ion is added to the system at constant 5 M ionic strength.[8] The chloride ion-dependent luminescence quantum yield,[9] determined by the quinine sulfate method,[10] and shown in Figure 1, first increases and then decreases at increasing chloride ion concentration, reaching a maximum value at about 3 M chloride ion. Time-resolved studies of the system on the nanosecond time scale[11] show that the luminescence lifetime increases with chloride ion concentration (Figure 1), behavior which can be explained by an equilibrated reaction among the excited copper(I) complex, ground-state chloride ion reactants, and an excited copper(I) species coordinated to the chloro ligand. The subsequent decrease in luminescence lifetime at higher

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(8) (a) Rather similar emission bands have been observed to appear in aqueous solutions of dihalocuprate(I) as halide ion concentration is increased.[8b-d] (b) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472. (c) Stevenson, K. L.; Berger, R. M.; Grush, M. M.; Stayanoff, J. C.; Horváth, A.; Horváth, O. *J. Photochem. Photobiol., A* **1991**, *60*, 215. (d) Horváth, O.; Stevenson, K. L.; Fendler, J. *Inorg. Chem.* **1993**, *32*, 227.
(9) Luminescence spectra were obtained on a Shimadzu RF-540 spectrofluorophotometer connected to an HP-86 microcomputer.
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(11) Time-resolved experiments were performed with a laser kinetic spectrometer (Applied Photophysics) previously reported.[8c]

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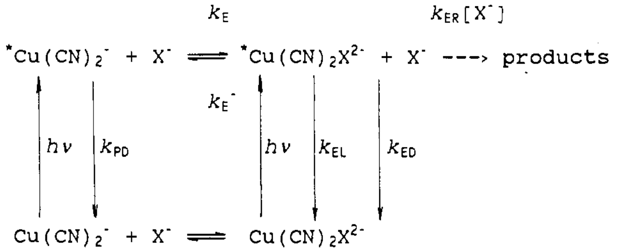
Scheme I[a]



[a] P = precursor, E = exciplex, D = nonradiative decay, L = luminescent decay, and R = reactive decay.

Table I. Rate Constants and the Formation Constant of the Exciplex Calculated from the τ-vs-$[X^-]$ Data Measured at Ambient Temperatures

rate const	X = Cl	X = Br	X = I
$10^{-7}k_{PD}$, s^{-1}	6.6 ± 0.4	6.3 ± 0.8	7.2 ± 1.1
$10^{-8}k_E$, $M^{-1}\ s^{-1}$	2.6 ± 0.2	14 ± 1	78 ± 4
$10^{-7}k_{E^-}$, s^{-1}	2.4 ± 0.2	5.2 ± 0.2	1.8 ± 0.1
$10^{-6}(k_{ED} + k_{EL})$, s^{-1}	4.7 ± 0.8	2.7 ± 0.1	4.5 ± 0.3
$10^{-6}k_{ER}$ s^{-1}	1.1 ± 0.2	0.7 ± 0.1	17 ± 1
K, M^{-1}	0.7 ± 0.12	2.5 ± 0.6	16 ± 4
$K_{EX} = k_E/k_{E^-}$, M^{-1}	11 ± 3	27 ± 4	430 ± 40

chloride concentrations, $[Cl^-] > 2.5$ M, suggests that the species $^*Cu(I)\cdots Cl^-$ is quenched by some bimolecular process involving chloride ion. Time-resolved absorption measurements reveal that there are short (several tens of nanoseconds) and a long-lived (several tens of microseconds) species absorbing between 300 and 450 nm. Since the lifetime of the former is identical to that of the 480-nm emission at various chloride concentrations, we infer that this absorption band is that of the luminescent species. The long-lived absorption band which peaks at 340 nm has not been identified.[12]

In principle, the luminescent species can be formed by excitation of either of the two equilibrated ground-state complexes, $Cu(CN)_2^-$ and $Cu(CN)_2Cl^{2-}$ ($K = 0.7 \pm 0.12$ M^{-1} [7]), since both absorb light in the UV. Scheme I shows that absorption by dicyanocuprate(I) leads to the formation of luminescent species via reaction between the excited dicyano complex and ground-state halide ion, whereas excitation of the mixed-ligand complex results in light-emitting species with no chemical reaction.[16] The general solution of such a coupled system results in a double-exponential function for time dependence of both the precursor and the luminescent species concentrations

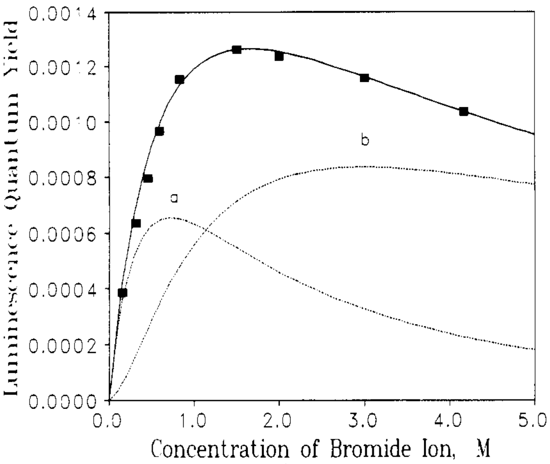


Figure 2. Dependence of luminescence quantum yield on bromide ion concentration at 5 M ionic strength: (■) measured; (—) calculated; (a) "partial" quantum yield derived from excitation of dicyanocuprate(I); (b) "partial" quantum yield derived from excitation of dicyanobromocuprate(I).

$$\tau_{1,2} = 2/\{(x + y) \bullet [(x - y)^2 + 4k_Ek_E^-[Cl^-]]^{1/2}\} \quad (1)$$

where $x = k_{PD} + k_E\,[Cl^-]$ and $y = k_{EL} + k_{ED} + k_{E^-} + k_{ER}[Cl^-]$. Since the fitting of a single-exponential function to the luminescence decay curve in the range where it does not coincide with the laser pulse (at halide ion concentrations where $\tau_2 > 30$ ns) is good, we conclude that the development of luminescence characterized by τ_1 is rather fast and is comparable to the pulse duration. Hence the rate constants involved in the mechanism can be estimated by fitting eq 1 to the τ_2-vs-halide ion concentration data using the Marquardt procedure.[14] The results are given in Table I.

A crucial point of the study was the verification of the luminescent exciplex and its precursor(s). Steady-state luminescence experiments resulted in a dependence of ϕ_L on halide ion concentration strongly resembling that in the chloride system, but with the maximum in ϕ_L appearing at smaller halide ion concentrations, especially in the case of iodide. Values obtained were $\phi_{L,max} = 6.3 \times 10^{-4}$, 1.25×10^{-3}, and 3.3×10^{-3} for $[Cl^-] = 2.45$ M, $[Br^-] = 1.65$ M, and $[I^-] = 0.16$ M, respectively. In addition, a red shift in the broad structureless emission was observed as the atomic weight of the halo ion was increased. All the rate constants (Table I) depend on the nature of the halide ion, except for k_{PD}, the values of which are identical within experimental error for all three systems. This suggests that Scheme I is essentially correct in describing the system since k_{PD} represents a pathway for decay of the single species $^*Cu(CN)_2^-$ which is the common to all three systems, whereas all the other rate constants are for pathways which are halide ion dependent.[15] The steady-state treatment of Scheme I gives an expression for the luminescence quantum yield, ϕ_L, consisting of two constituents, *a* and *b*, which arise from the coincident excitation of the dicyanocuprate(I) and chlorodicyanocuprate(I) complexes:

$$\phi_L = \phi_2k_{EL}f_2k_E[X^-]/(xy - k_Ek_E^-[X^-]) + \phi_3k_{EL}f_3x/(xy - k_Ek_E^-[X^-]) = a + b \quad (2)$$

where f_2 and f_3 are the fractions of light absorbed by $Cu(CN)_2^-$ and $Cu(CN)_2X^{2-}$, respectively, and ϕ_2 and ϕ_3 are the quantum yields for formation of the exciplex precursor, $^*Cu(CN)_2^-$, and of $^*Cu(CN)_2X^{2-}$, which could be either a triscoordinated exciplex precursor or the exciplex itself. Both partial luminescence quantum yields, *a* and *b*, depend on the halide ion concentration and exhibit maxima at different halide ion concentrations, as

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(12) (a) This band resembles the absorption spectrum of the $^{\bullet}Cl_2^-$ radical,[12b] which could be formed via a redox quenching reaction postulated above. The copper(0) complexes, which could originate from a reaction between ground-state copper(I) and the solvated electron ejected from the UV-excited Cu(I) complex,[12c] also have a similar absorption band in this range.[12d] Although formation of a hydride from photoexcited copper(I) complexes is favored in solutions of high $[H^+]$, hydrides can be ruled out since our experiments were carried out at pH >7. (b) Jayson, G. G.; Parson, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1597. (c) Horvâth, A.; Horvâth, O.; Stevenson, K. L. *J. Photochem. Photobiol., A* **1992**, *68*, 155. (d) Sukhov, N. L.; Akinshin, M. A.; Ershov, B. G. *High Energy Chem.* (*Engl. Transl.*) **1986**, *20*, 303.

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(15) Further support for this conclusion comes from our preliminary results from the $CuCl_2^-$–Cl^- and $CuBr_2^-$–Br^- systems, the luminescent lifetimes of which also depend on halide ion concentration. However, by applying our same methods of rate constant estimation, we obtained rather different k_{PD} values (3.6×10^8 and 2.2×10^8 $M^{-1}\ s^{-1}$ for chloride and bromide, respectively), consistent with the fact that the exciplex precursors in this case are different excited halocuprate(I) species.

(16) It should be noted that UV excitation of both complexes, $Cu(CN)_2^-$ and $Cu(CN)_2X^{2-}$, leads to electron ejection with different quantum yields.[12c] Hence we surmise that the solvated electron formation from an excited state of a higher energy level occurs on the picosecond or sub-picosecond time scale in competition with the creation of the precursor, $^*Cu(CN)_2^-$, and the luminescent species, $^*Cu(CN)_2X^{2-}$, of lower energy respectively, via internal conversion (IC).

shown in Figure 2.[17] The position of these maxima are dependent on the rate constants of Scheme I, the molar absorption coefficients of the two complexes, and the stepwise formation constant, *K*, but they are not dependent on ϕ_2 and ϕ_3. The good fit of eq 2 to the measured quantum yields confirms that two pathways, i.e. excitations of both the dicyano and the mixed-ligand complexes, are effective in producing the luminescent exciplex,[18] according to Scheme I.

We have found that increasing the cyanide ion concentration in solutions of the $Cu(CN)_2^-$- - -Cl^- system causes static quenching of the exciplex emission,[19] which indicates that the excited tricyanocuprate(I) cannot form an exciplex with chloride ion, confirming that exciplex formation is favored when arising from a coordinatively unsaturated excited state. Addition of electron-donor molecules such as CH_3CN and DMSO to the luminescent solution results in the dynamic quenching of the exciplex. The quenching constants in solution of 5 M Cl^- have values ($k_q = (4.6 \pm 0.4) \times 10^7$ and $(3.5 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for CH_3CN and DMSO, respectively) which are rather similar to those obtained for quenching of $^*Cu(dmp)_2^+$,[2,3,20] from which the intrinsic rate constant for quenching of a triplet CT state was predicted.

The temperature dependence of luminescence has also been studied. We found that the lifetime decreases with temperature at any halide concentration. At a series of temperatures, isothermal τ-vs-$[X^-]$ data were used to calculate, by the procedure mentioned above, the various rate constants in Scheme I, from which linear Eyring plots were used to calculate the enthalpy and entropy of activation for the different formation and decay pathways. Both the small negative enthalpy of activation (e.g. $\Delta H^\ddagger_E = -3 \pm 2$ kJ mol^{-1}, when X = Cl) and the large negative entropy of activation (e.g. $\Delta S^\ddagger_E = -89 \pm 6$ J mol^{-1} K^{-1}, when X = Cl) for the reaction resulting in the luminescent species can be regarded as another indication of the exciplex formation.[2,3] The negative entropy of activation for the exciplex reactions (e.g., when X = Cl: exciplex back-reaction, $\Delta S^\ddagger_{-E} = -54 \pm 4$ J mol^{-1} K^{-1}; nonradiative decay of exciplex, $\Delta S^\ddagger_{ED} = -69 \pm 5$ J mol^{-1} K^{-1}, reactive decay of exciplex, $\Delta S^\ddagger_{ER} = -58 \pm 5$ J mol^{-1} K^{-1}) suggests that solvation plays an important role in these processes.

Our work shows direct spectroscopic and kinetic evidence that the excited copper(I) central atom in an extremely unsaturated coordination sphere can form a luminescent exciplex even in a highly polar medium such as water. Coordination of the halide ion to $^*Cu(CN)_2^-$ is forced by the interaction between the unfilled acceptor orbital of the central copper atom and the halide ion as donor constituent and by an electrostatic attraction of the metal center, considered to be Cu(II) after excitation. Since the coordination sphere of $^*Cu(CN)_2X^{2-}$ is still not completely saturated, it is reasonable to suspect that there could be a transition state with a coordination number of 4, which is more common for copper(II) species. The temperature dependence of the reaction kinetics reflects activation enthalpy and entropy values[23] which also support the proposed mechanism involving a luminescent inorganic exciplex. Detailed studies of these systems are in progress.

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(17) It can be shown that at high $[Cl^-]$, $\phi_L/\tau \rightarrow k_{EL}\phi_3$. Thus, from the asymptote of the plot of ϕ_L/τ vs $[Cl^-]$ (Figure 1) a value of 6800 s^{-1} was estimated for $k_{EL}\phi_3$, allowing for a plot of *b*. A value of ϕ_3/ϕ_2 (0.8) was then estimated which gave the best fit of eq 2 to the quantum yield data of Figure 2, from which the plot of *a* was then obtained by subtracting *b* from ϕ_L.

(18) (a) Our designation of the luminescent copper(I) species as an exciplex is consistent with the general concept of excited complexes: "Many molecules that do not interact significantly in their ground states appear to form reasonably stable complexes when excited. The complexes are called excimers and exciplexes."[18b] Since we consider an excited complex which does not have a corresponding ground state as an ideal but not exclusive example of an exciplex, we regard the species $^*Cu(CN)_2X^{2-}$ as exciplexes because their stepwise formation constants are larger than those of the corresponding ground-state complexes. The recent systematic study of the well-known pyrene excimer in cyclohexane[18c] compares the formation constant of the dimer in the ground state with that of the excimer. (b) Wayne, R. P. *Principles and Applications of Photochemistry*; Oxford University Press; Oxford: U.K., 1988; p 111. (c) Adriensen, R.; Ameloot, M.; Boens, N.; De Schryver, F. C. *J. Phys. Chem.* **1992**, *96*, 314.

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