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Luminescence and Ultraviolet Photoinduced Electron Transfer in Chlorocuprate(I) Complexes in Aqueous Solution at Room Temperature

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Excitation of the CTTS bands of $\mathrm{CuCl_2^-}$ and $\mathrm{CuCl_3^{2-}}$ ions at 274 nm, in neutral aqueous solutions containing 5 M chloride ion at room temperature, results in luminescence emission centered at 470–480 nm, with a quantum yield of 3.6×10^{-3} and a lifetime of 105 ns. The luminescence is quenched by hydrogen ions and obeys a linear Stern–Volmer relationship, yielding a value for a second-order quenching rate constant of 5.8×10^8 $\mathrm{M^{-1}\ s^{-1}}$. Reduced ionic strength and chloride ion inhibit the luminescence. The photooxidation of these complexes and production of hydrogen gas by continuous irradiation of the CTTS band are shown to be inhibited by increased ionic strength and chloride ion. This behavior is explained in terms of a proposed photophysical mechanism in which hydrated electron formation competes with the decay of the CTTS excited state to an emitting spin-forbidden state.

Introduction

Copper(I) complexes, because of their d^{10} electron configuration, are lacking in ligand-field absorption bands; hence, absorption of light results in promotion of the electron to energy states that are often capable of undergoing electron-transfer reactions. For example, a great deal of photochemistry involving metal-to-ligand-charge-transfer (MLCT) bands in copper(I) complexes containing substituted 1,10-phenanthroline ligands has been studied by McMillin and co-workers, who have observed photoinduced electron transfer to cobalt(III) complexes in aqueous solution,[4,5] luminescence in glasses and organic solvents,[6] and evidence for inorganic exciplex formation.[7,8]

Our work, on the other hand, has been focused on the photoinduced electron transfer in copper(I) complexes having halo or ammine σ-donor ligands, in which MLCT transitions are less likely. In our earlier studies of chlorocuprate(I) complexes,[9-13] we have shown that in aqueous solutions containing chloride ligand and copper(I) chloride at concentrations of 0.01 M and below, the two stable copper complexes, $\mathrm{CuCl_2^-}$ and $\mathrm{CuCl_3^{2-}}$, are photooxidized in the presence of electron scavengers such as $\mathrm{H^+}$ and $\mathrm{N_2O}$ when irradiated in the ultraviolet region corresponding to a charge-transfer-to-solvent (CTTS) transition centered at 274–276 nm. The overall reaction is

$$\mathrm{CuCl}_n^{1-n} + \mathrm{H}^+ = \mathrm{CuCl}_n^{2-n} + \tfrac{1}{2}\mathrm{H}_2(\mathrm{g}) \qquad (1)$$

and proceeds by a mechanism involving hydrated electrons.[11,12,14] The half-order dependence of the quantum yield on scavenger concentration led us to propose the geminate-pair scavenging mechanism observed in the CTTS excitation of halide ions.[15-17] Studies by Horvath and Papp[18] and by us[19] suggested that the dichloro complex, which has a lower oscillator strength than the trichloro species, has the higher quantum yield for photooxidation.

In this report we describe the dependencies of the room-temperature photoluminescence quantum yield and lifetime on ligand concentration and ionic strength, along with a proton-quenching study of the quantum yield, and we contrast the effects of ionic strength and ligand concentration on the spectra and photoactivities of the two complexes. The results of these studies suggest some new insights into the photophysical processes occurring in copper(I) complexes upon absorption of light.

Experimental Section

Materials. All solutions were prepared from reagent grade NaCl, HCl, $\mathrm{NaClO_4}$, or $\mathrm{HClO_4}$ and CuCl, prepared and purified as described previously.[11]

Procedures. Stock solutions of NaCl, HCl, $\mathrm{NaClO_4}$, and $\mathrm{HClO_4}$ were standardized by usual analytical procedures, except for $\mathrm{NaClO_4}$, which was standardized by density. For most of the photochemical runs and absorption spectra, the hydrogen ion concentration was fixed at 1 M by using either of the two acids. Ionic strength and ligand concentration were adjusted by appropriate mixtures of the stock solutions, ignoring the effect of the formation of the copper complexes on ligand concentration and ionic strength when total copper concentration was less than 1% of the ligand concentration.

Solutions were prepared for spectra as described previously[11] and experiments were run in a computer-interfaced Beckman ACTA M-VI spectrophotometer[20] in calibrated 0.01-cm cuvettes obtained from Precision Cells and thermostated at 25 °C. Similarly, dilute degassed solutions of CuCl were prepared for the luminescence spectra, and experiments were run in 1-cm cuvettes in a Shimadzu RF-540 spectrofluorometer. Definitive luminescence spectra were obtained on freshly prepared solutions of CuCl having an optical density adjusted to 0.5 in conjunction with an HP 8451 diode-array spectrophotometer. A Beer's law study indicated that the emission intensities at all wavelengths are proportional to concentration in this optical density range.

The quantum yield of luminescence was determined by comparing the emission intensities at 475 nm for the copper complexes in 5 M NaCl medium with that of quinine bisulfate, which has a quantum yield of 0.55.[21] Since the optimum excitation wavelength of the copper complexes (274 nm) is different from that of quinine bisulfate (348 nm), the comparison was made on solutions having optical densities of 0.048 at their excitation wavelengths, and the ratio of the emission intensities was corrected for the different intensities of the source at the two excitation wavelengths by calibration with a potassium tris(oxalato)ferrate (III) actinometer.[22]

In the studies of the effects of ligand concentration, ionic strength, and hydronium ion concentration on luminescence, solutions having optical densities in the 0.5–1.0 range were used. In any given set of runs, the absorption spectra of all samples were virtually identical, such that the intensities of emission should have all been proportional to quantum yield.

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Table I. Equilibrium Constants and Absorption Maxima of $CuCl_2^-$ and $CuCl_3^{2-}$ at 1 and 5 M Ionic Strength and 1 M H^+

ionic strength	complex	*K*	λ, nm	*e*	λ, nm	*e*
1.0	$CuCl_2^-$	0.656	233	943	274	186[b]
	$CuCl_3^{2-}$		230	1640[b]	276	3720
5.0	$CuCl_2^-$	0.648[a]	231	1030	274	513[b]
	$CuCl_3^{2-}$		230	1670[b]	274	4920

[a] This compares to 0.763 obtained by Ahrland and Tagesson.[24]
[b] This is a shoulder.

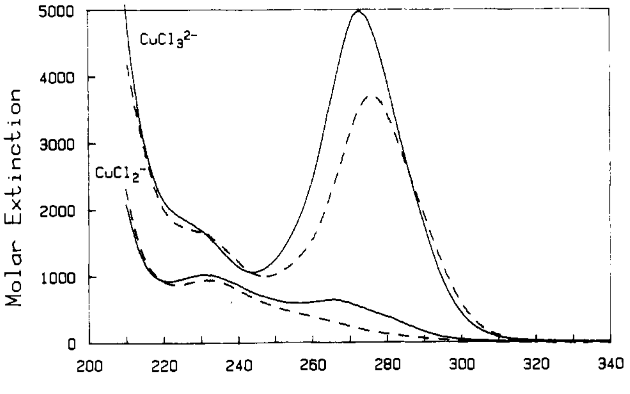

Figure 1. Resolved ultraviolet absorption spectra of $CuCl_2^-$ and $CuCl_3^{2-}$ in (- - -) 1 M and (—) 5 M ionic strength aqueous solution; perchlorate medium, both at $[H^+] = 1$ M.

These intensities were converted to quantum yield by normalization to the value obtained above.

Luminescence lifetimes were determined by utilizing the 265-nm, frequency-quadrupled output from a QuantaRay Nd YAG laser of 8-ns pulse width, in the laboratory of Clifford P. Kubiak.

Continuous photolysis runs were performed by measuring the volume of hydrogen evolved over time, with a microvolumeter,[23] and quantum yields were determined from hydrogen evolution rates and light intensity measurements obtained actinometrically as described above.

Results and Discussion

Absorption Spectra. Equilibrium constants were determined for the monomer equilibrium

$$CuCl_2^- + Cl^- = CuCl_3^{2-} \qquad (2)$$

at 1 and 5 M ionic strength and 1 M hydrogen ion concentration by using a spectrometric procedure described previously[11] and by utilizing the expression

$$e = e_3 + (e_2 - e_3)/(1 + K[Cl^-]) \qquad (3)$$

At the copper concentrations used in these studies, there is no spectral evidence for the existence of any polynuclear species. Table I summarizes the values of *K*, for reaction 2, and the extinction coefficients, *e*, at the wavelength maxima obtained for the two complexes at the two ionic strengths. Figure 1 shows the resolved spectra of the chloro species at 1 and 5 M ionic strength.

It is apparent from these spectra that coordination number, and, to a lesser extent, ionic strength play a significant role in the oscillator strengths of the two bands in the 220–300-nm region: one at 225–240 nm and the other at 265–280 nm, which we have previously assigned as CTTS and the one responsible for photochemical hydrated electron formation.[11] The published spectra of the dichloro complex at lower ionic strengths have not clearly indicated existence of this band,[11,25,26,18] but Figure 1 shows that it does appear as a distinct band at 5 M ionic strength.

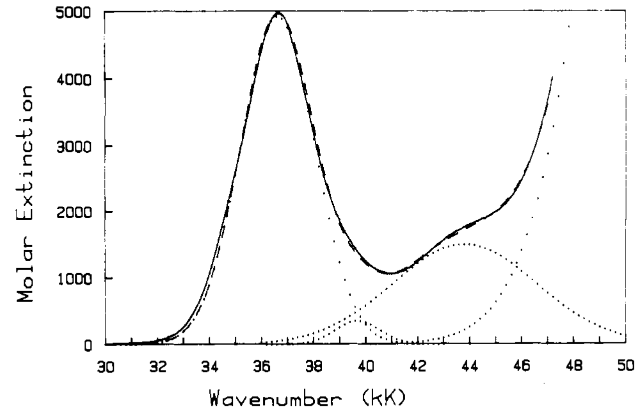

Figure 2. Resolved Gaussian absorption bands of $CuCl_3^{2-}$ at 5 M ionic strength, from Figure 1: (—) measured spectrum; (···) resolved bands; (- - -) sum of resolved bands.

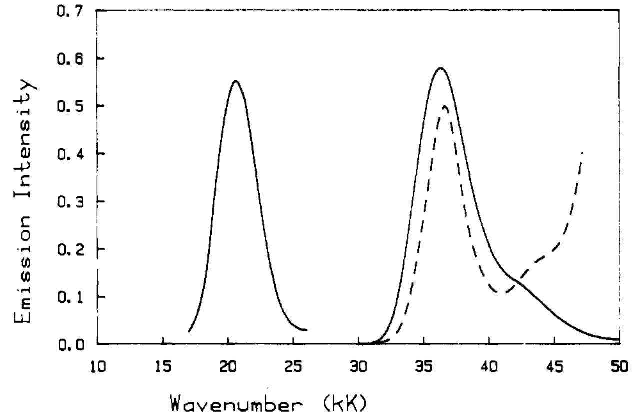

Figure 3. Luminescence excitation spectrum monitored at 21.0×10^3 cm^{-1} (475 nm) and emission spectrum excited at 36.5×10^3 cm^{-1} (274 nm) of 1.3×10^{-4} M CuCl in 5 M NaCl at room temperature (—) and molar absorption spectrum of $CuCl_3^{2-} \times 10^{-4}$ (- - -).

Table II. Oscillator Strengths and Estimated Radiative Lifetimes of the 274–276-nm Absorption Band for the Two Copper Complexes in 1 M H^+ and 1 and 5 M Ionic Strength

ionic strength	complex	osc strength	radiative lifetime, ns
1.0	$CuCl_2^-$	0.00164	670
	$CuCl_3^{2-}$	0.0439	26
5.0	$CuCl_2^-$	0.00595	180
	$CuCl_3^{2-}$	0.0586	19

Figure 2 is a replotting of the spectrum of $CuCl_3^{2-}$ with the abscissa linear in energy allowing for resolution into Gaussian-shaped bands for determining oscillator strengths. A computer found the best values of the maximum extinction coefficient (e_0), the wavenumber maximum (ν_1), and the half-bandwidth (γ_D) in the expression for Doppler-broadened absorption bands[27]

$$e = e_0 \exp[-(\nu - \nu_1)^2(\ln 2)/(\gamma_D/2)^2] \qquad (4)$$

which fit the actual absorption spectrum. A good fit necessitated the use of four bands, which included a very weak band centered at about 250 nm. The oscillator strength, *f*, is given by[28]

$$f = 4.319 \times 10^{-9} \int e \, d\nu = 4.319 \times 10^{-9}[(\gamma_D/2) \ln 2]^{1/2} \qquad (5)$$

obtained from the integral of eq 4. The radiative lifetime, τ, is estimated from the relation[29]

$$\tau = 1.5/f\nu^2 \qquad (6)$$

which assumes equal degeneracies for the ground and excited states. This procedure was performed on all four spectra of Figure 1, and the results are shown in Table II.

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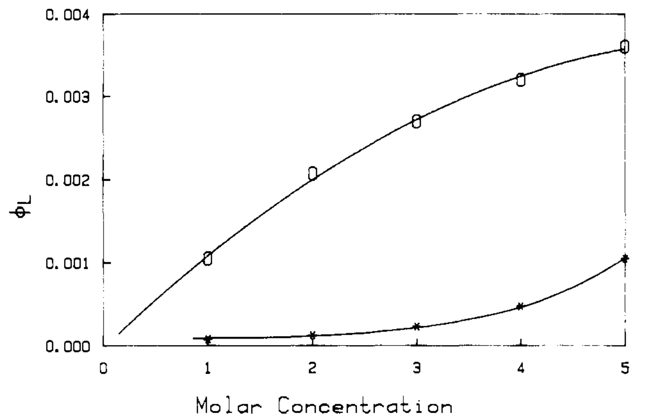

Figure 4. Quantum yield of luminescence versus chloride concentration (O) at 5 M ionic strength or versus ionic strength (*) at 1 M chloride concentration, for neutral CuCl solutions with optical density = 0.95 at 274 nm.

Table III. Measured Luminescence Decay Liftimes as a Function of Ionic Strength and Chloride Concentration for a CuCl Solution with Optical Density of 0.7 at Excitation Wavelength 266 nm

ionic strength	[Cl⁻], M	lifetime, ns
5	5	105
5	1	44
1	1	9.8

Luminescence. The excitation and emission spectra (in terms of wavenumber) for the luminescence of a 1.3×10^{-4} M solution of CuCl in neutral 5 M NaCl at room temperature are shown in Figure 3, with the absorption spectrum of $CuCl_3^{2-}$ superimposed on the excitation spectrum, clearly showing the correlation between absorption and excitation. While it is apparent that excitation of the CTTS band leads to most of the emission, the higher energy absorption (at 235 nm or 42 500 cm^{-1}) also produces some luminescence, as indicated by the shoulder on the excitation band. Measurement of the quantum yield of emission yielded a value for this solution of 3.6×10^{-3}.

The emission was reduced by a decrease in chloride concentration, at 5 M ionic strength, and by a decrease in ionic strength, at 1 M chloride concentration, as indicated in Figure 4, which shows the quantum yields versus concentration for both chloride and ionic strength.

The measured lifetimes were also functions of ionic strength and chloride concentration as indicated in Table III. If the luminescence were to originate from the same CTTS state that gives rise to the absorption at 274 nm, then the simple relationship for quantum yield would apply:

$$\phi_L = k_L/(k_L + k_{NR}) \qquad (7)$$

where k_L and k_{NR} represent the first-order rate constants for luminescence and the other nonradiative decay processes, respectively. Since the measured lifetime for the luminescent species would be the reciprocal of the sum of the first-order decay constants ($k_L + k_{NR}$), the true luminescence lifetime ($1/k_L$) would be easily calculated from the quantum yield measurements, giving 2.9×10^{-5}, 4.2×10^{-5}, and 1.3×10^{-4} s for the three solutions, respectively. Because these values are 2–3 orders of magnitude larger than the estimated radiative lifetimes of the CTTS state given in Table II, it is concluded that the emitting state is *not* the CTTS state, a result that is consistent also with the rather large Stokes shift of about 15 000 cm^{-1} for the luminescence. Since there are no absorption bands at longer wavelengths other than the CTTS band, it is reasonable to suggest that the emitting state is a spin-forbidden triplet state.

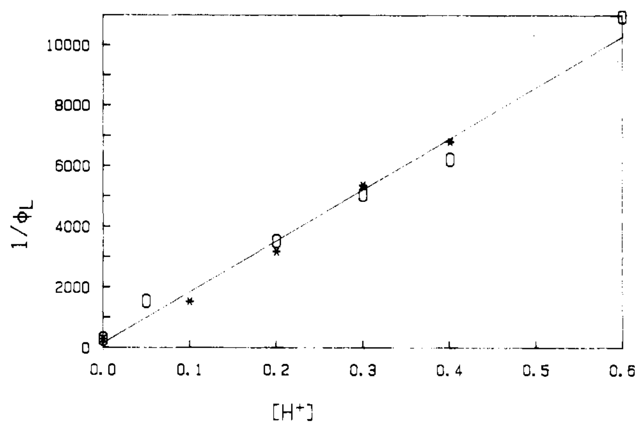

Figure 5. Stern–Volmer plot for quenching of luminescence by H⁺ for solutions containing CuCl at concentrations of 2.5×10^{-4} M (O) and 1.3×10^{-4} M (*) in 5 M Cl⁻ at room temperature.

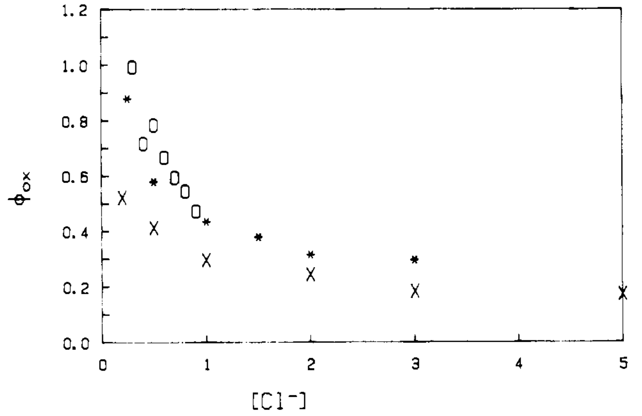

Figure 6. Quantum yield of photooxidation (eq 1) versus chloride ion concentration of 0.01 M CuCl solutions at [H⁺] = 1 M for (O) 1 M, (*) 3 M (from ref 11), and (X) 5 M ionic strength.

Hydrogen ion quenches the luminescence according to a linear Stern–Volmer relationship

$$1/\phi = A + B[H^+] \qquad (8)$$

where A and B are experimental constants. A Stern–Volmer plot is shown in Figure 5 for a 5 M Cl⁻ solution at an excitation wavelength of 274 nm. Assuming that the luminescence originates from some state for which the quantum yield of population is ϕ_T and that protons react with this state, then the observed quantum yield of luminescence should be

$$\phi = \phi_T k_L/(k_L + k_{NR} + k_H[H^+]) \qquad (9)$$

where k_H is a second-order rate constant for the reaction. Thus the constants A and B can be identified with the quantities $(k_L + k_{NR})/\phi_T k_L$ and $k_H/\phi_T k_L$, respectively, and B/A results in the value for k_H. From the slope of the plot in Figure 5 for B and the value of $1/\phi$ for the neutral solution for A, a value for k_H of 5.8×10^8 M^{-1} s^{-1} is obtained.

Photoinduced Electron Transfer. Figure 6 shows the chloride ion dependence of quantum yield of dihydrogen production for continuous photolysis at 274 nm, according to the stoichiometry of eq 1 for solutions containing 0.01 M CuCl and 1 M H⁺ and having the three ionic strengths 1, 3, and 5 M. Two explanations have been advanced for previous observations of a decline in measured quantum yield with chloride concentration: the individual quantum yield of $CuCl_2^-$ may be greater than that of $CuCl_3^{2-}$, which is favored by the shifting equilibrium at higher chloride concentration,[18,19] or, alternatively, the individual quantum yield of $CuCl_3^{2-}$ may be affected by the change in medium as the relative amounts of chloride and perchlorate are varied in order to maintain constant ionic strength.[11] In fact, the data suggest that both factors may be important.

This can be seen by considering that the measured quantum yield is given by

$$\phi = f_2\phi_2 + f_3\phi_3 \qquad (10)$$

where f_2 and f_3 are the fractions of light absorbed by each complex

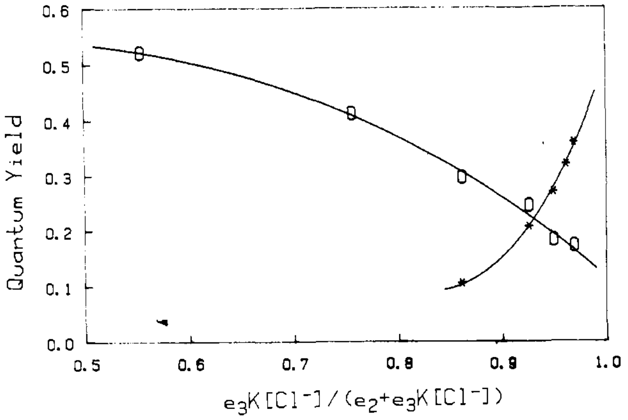

Figure 7. (○) Quantum yield for photooxidation or (*) quantum yield × 100 for luminescence versus fraction of light absorbed by $CuCl_3^{2-}$ at 5 M ionic strength (data from Figures 4 and 6).

and are equivalent to the ratio of the absorbance of that complex to the total absorbance and ϕ_2 and ϕ_3 are the individual quantum yields of the complexes.[18] Since the sum of the fractions of light absorbed by each complex is unity, eq 10 becomes

$$\phi = \phi_2 + (\phi_3 - \phi_2)f_3 = \phi_3 + (\phi_2 - \phi_3)f_2 \qquad (11)$$

so that a plot of ϕ vs either f_2 or f_3 should give a straight line for the case of an equilibrium shift between invariant quantum yields, or curves if the individual quantum yields are affected by the ionic medium. Figure 7 shows plots of quantum yields for both photoxidation and photoluminescence (×100) versus fraction of light absorbed by the trichloro complex, at 5 M ionic strength. The curvature of these plots suggests that there are indeed medium effects on the individual quantum yields of $CuCl_2^-$ and $CuCl_3^{2-}$ for both photooxidation and luminescence, with chloride ion playing a larger role than perchlorate in inhibiting photooxidation while promoting photoluminescence. In spite of the difficulty in separating the individual quantum yields, extrapolation of the plots to either $f_3 = 0$ or $f_3 = 1$ indicates that the trichloro species is probably the only photoluminescent complex in the system, whereas both complexes undergo photooxidation, with the dichloro complex being more photoactive than the trichloro species.

Thus, it would appear that the parameters which tend to enhance the photooxidation, such as stereochemistry (i.e. the linear $CuCl_2^-$ ion versus the trigonal planar $CuCl_3^{2-}$ ion[30]), low ionic strength, and low chloride ion medium, tend to suppress the photoluminescence, suggesting that photooxidation and luminescence are competitive pathways for discharging the energy of the excited copper complexes.

In our earlier work[11,12] we showed that hydrated electrons were formed following absorption of light, and we explained the half-order dependence of quantum yield of photooxidation on hydronium ion in terms of the geminate-pair scavenging theories of Noyes[15,16] and Jortner et al.[17] Our estimate of the rate constants for hydronium geminate-pair scavenging was 1–2 orders of magnitude greater than the value of k_H listed above for hydronium quenching of luminescence, which appears to occur through a simple second-order process. Thus, we conclude that these are two distinct scavenging processes.

Although the UV absorption at 274 nm has been designated CTTS,[11] other workers have attributed very similar absorption bands coupled with luminescence in other Cu(I) systems strongly resembling this one to excitation to a d^9s^1 metal-centered state. For example, the room temperature absorption of benzene solutions of the tetramers $(CuLI)_4$ (L = pyridine or morpholine) occurs at wavelengths below 313 nm and results in luminescence at 600–700 nm.[31] This is attributed to transition to the metal-centered state, d^9s^1, followed by decay to a spin-forbidden state from which the luminescence originates, on the basis of the large Stokes shifts (ca. 19 × 10^3 cm^{-1}) and long luminescence lifetimes (300–900 ns). The abscrptions of copper-doped crystals of NaCl and other halides and of copper-doped glasses show a band at about 260–270 nm[32-35] resulting in luminescence, and in most cases this has been explained in terms of an initial excitation of the Cu^+ ion to the d^9s^1 state. Because the electron excited to d^9s^1 would occupy a larger, spherical, and more diffuse s orbital than the d orbital in the d^{10} ground-state, it is very tempting to suggest that both d^9s^1 and CTTS are descriptions of the primary geminate pair.

These examples indicate that Cu(I) has a relatively long-lived state from which luminescence can occur after excitation of what is essentially an atomic transition. However, in aqueous solution occupation of this spin-forbidden state is low due to the efficient charge-transfer quenching and nonradiative secondary recombination reactions.

A mechanism that seems consistent with these observations is shown in Scheme I.

Scheme I

$CuCl_n^{1-n} \xrightarrow{h\nu} [CuCl_n^{1-n}]^*$	UV excitation to d^9s^1 = CTTS = singlet primary geminate pair (^{1}PGP)
$^1PGP \xrightarrow{k_D} {}^1SGP$	secondary geminate pair formation
$^1SGP + H^+ \xrightarrow{k_s} CuCl_n^{2-n} + H^\bullet$	singlet secondary pair scavenging
$^1SGP \xrightarrow{k_r} CuCl_n^{1-n}$	singlet secondary pair recombination
$^1SGP \xrightarrow{k_e} CuCl_n^{2-n} + e_{aq}^-$	aquated electron formation
$^1SGP \xrightarrow{k_{isc}} {}^3CuCl_n^{1-n}$	"intersystem crossing" or spin unpairing
$^3CuCl_n^{1-n} + H^+ \xrightarrow{k_H} CuCl_n^{2-n} + H^\bullet$	luminescence quenching by hydronium ion
$^3CuCl_n^{1-n} \xrightarrow{k_L} CuCl_n^{1-n}$	luminescence of spin-forbidden state
$^3CuCl_n^{1-n} \xrightarrow{k_{NR}} CuCl_n^{1-n}$	nonradiative deactivation of spin-forbidden state

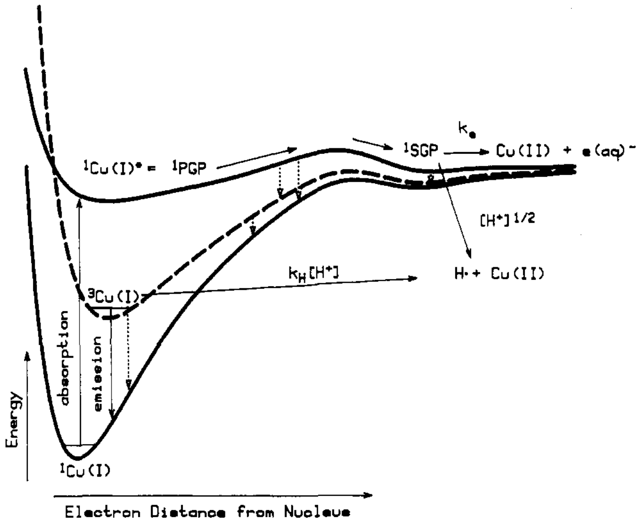

Figure 8. Proposed energy level diagram.

Figure 8 is a proposed energy diagram illustrating the various reaction pathways for this system. We have drawn the energy curves such that as the separation of the Cu(II) atom and the electron approach infinity, they have the same energy regardless of the electronic state. Absorption of light excites the Cu(I)

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complex to the singlet primary geminate pair (^{1}PGP). Although the electron may have enough energy to dissociate to the singlet secondary geminate pair (^{1}SGP), it must first traverse an energy barrier that is affected by the solvent dielectric and transport properties. Since recent evidence shows that electrons move through water by a Grotthus mechanism,[36] influences that disrupt the structure of water, such as a highly ionic medium, would inhibit the mobility of electrons to form the ^{1}SGP, increasing the likelihood of decay either to the triplet state (intersystem crossing), resulting in luminescence, or back to the ground-state energy curve (primary pair recombination). Once the ^{1}SGP is reached, the previously observed[11] reactive-scavenging kinetics, which includes secondary pair recombination, half-order hydronium ion scavenging, and hydrated electrons escaping secondary recombination or scavenging, becomes operative. Apparently, such a reactive-scavenging kinetic scheme is not observed for hydronium ion quenching of the luminescence probably because the lifetime of the triplet state is long enough to permit the slower conventional second-order kinetics observed.

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Registry No. $\mathrm{CuCl_2^-}$, 15697-16-2; $\mathrm{CuCl_3^{2-}}$, 29931-61-1; $\mathrm{Cl^-}$, 16887-00-6; $\mathrm{H^+}$, 21408-02-5; $\mathrm{H_2}$, 1333-74-0.

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Rotational Strengths of Sharp-Line Electronic Transitions of Tris(ethylenediamine)chromium(III)

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A method has been developed to calculate relative rotational strengths for transition-metal complexes based on the actual geometry of the ligating atoms and any other atoms contributing to the molecular dissymmetry. Such calculations are particularly useful in the analysis of sharp-line phenomena in circular dichroism spectra, since narrow CD peaks often represent single, nondegenerate electronic transitions. This approach was used to examine a controversy over the splitting of the $^2\mathrm{T}_{1g}$ components in $[\mathrm{Cr(en)_3}]^{3+}$ arising from quite different assignments in single-crystal and solution spectra. Calculations suggest that both assignments are correct. One reason for the discrepancy appears to be that the twist angle of the nitrogen coordination sphere is closer to that of an octahedron in solution than in the crystal, leading to a larger $^2\mathrm{T}_{1g}$ splitting. The calculations also indicate that the chelate ring conformation in solution is *lel*$_2$*ob*, as it is also (predominantly) in crystalline $[\mathrm{Cr(en)_3}]\mathrm{Cl_3}$. The marked sensitivity of the calculated signs and magnitudes of the sharp-line CD peaks to the twist angle of the complex was instrumental in reaching these conclusions.

Introduction

In an isotropic collection of chiral molecules the rotatory strength of an electronic transition from the ground state, ψ_0, to an excited eigenstate, ψ_j, is related to the product of the electric dipole and magnetic dipole transition moments between the two states[1]

$$R(0\rightarrow j) = \mathrm{Im}[\langle\psi_0|\mathbf{Q}|\psi_j\rangle\cdot\langle\psi_j|\mathbf{M}|\psi_0\rangle] \tag{1}$$

where **Q** and **M** are the electric and magnetic dipole operators, respectively. Im denotes the imaginary part of the complex expression. The dot indicates that the rotational strength is a pseudoscalar product, i.e., that the rotational strength depends on the cosine of the angle between the electric and magnetic moment vectors.

$$R(0\rightarrow j) = \mathrm{Im}[\langle\psi_0|Q_x|\psi_j\rangle\langle\psi_j|M_x|\psi_0\rangle + \langle\psi_0|Q_y|\psi_j\rangle \langle\psi_j|M_y|\psi_0\rangle + \langle\psi_0|Q_z|\psi_j\rangle\langle\psi_j|M_z|\psi_0\rangle] \tag{2}$$

The rotational strength is directly proportional to the area under the corresponding circular dichroism (CD) band.[2,3]

The one-electron electric dipole operator is proportional to the position vector **r**, and the magnetic dipole operator to the orbital and spin angular momenta, **l** and **s**.

$$\mathbf{Q} = e_{\mathrm{el}}\mathbf{r} \qquad \mathbf{M} = \frac{e_{\mathrm{el}}}{2mc}(\mathbf{l} + 2\mathbf{s}) \tag{3}$$

where m is the mass of and e_{el} is the charge on an electron.[4]

Moffitt[5] was the first to use a ligand field model to evaluate eq 2 for transition-metal complexes. There are three elements in the construction of a model to use eq 2 to calculate rotational strengths for metal complexes: how the wave functions are to be defined, and how the electric and magnetic dipole matrix elements are to be evaluated. There have been two distinct approaches to the definition of the wave functions. One is to use orbital wave functions, allowing the ready evaluation of electric and magnetic transition dipole matrices from the properties of atomic orbitals. The wave functions are then, directly or indirectly, linear combinations of multielectron atomic orbital basis functions.

The second approach is to ignore the orbital composition of the multielectron wave functions and instead to identify them by group representation labels. Electric and magnetic dipole matrices can then be constructed by means of vector coupling coefficients. This approach is only useful when the symmetry of the functions used is high and is most powerful when octahedral wave functions are employed. This takes maximum advantage of group-theoretical methods, but since electric dipole matrix elements are zero between the eigenfunctions of d^n in O_h symmetry (i.e. O_h molecules are optically inactive), a lower-symmetry field must be introduced as a perturbation.

Moffitt used, implicitly, orbital wave functions, concentrating on the one-electron transition responsible for the spin-allowed bands in Cr(III) and Co(III) complexes. The problem he then faced has remained a fundamental concern in all subsequent models. When d wave functions are used in the basis set, the magnetic moment integrals can be evaluated straightforwardly,

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