Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Photostudies of Copper(I) Systems. 6. Room-Temperature Emission and Quenching Studies of $[Cu(dmp)_2]^+$

MARCUS W. BLASKIE and DAVID R. McMILLIN*

Received April 17, 1980

Photoluminescence from bis(2,9-dimethyl-1,10-phenanthroline)copper(I) has been observed at room temperature in CH_2Cl_2. The lifetime of the emission is 54 ± 10 ns, and the quantum yield of emission is about 2×10^{-4}. The corrected emission spectrum is broad and structureless, maximizing at 730 nm, and is attributed to a metal-to-ligand charge-transfer excited state. Quenching studies with a series of substituted nitrobenzene derivatives suggest that the excited state has a reduction potential of about $\lesssim -1.4$ vs. SCE; hence most of the energy of the excited state is available as electrochemical potential. No emission from the complex could be detected in methanol, ethanol, or acetonitrile. Moreover, addition of the latter species leads to a diminution of the emission which is observed in CH_2Cl_2. Possible physicochemical interactions that could give rise to the latter effect are considered.

Introduction

Recently there has been considerable interest in the bimolecular reactivity of photoexcited states of transition-metal complexes.[1] These species can participate in a number of interesting redox processes including H_2 formation.[2] One view[3]—not shared unanimously[4]—is that such systems may ultimately prove useful in solar energy conversion.

We have found that exciting the low-lying metal-to-ligand charge-transfer (MLCT) state of bis(2,9-dimethyl-1,10-phenanthroline)copper(I), abbreviated $[Cu(dmp)_2]^+$, in the presence of a variety of Co(III) substrates leads to net electron transfer with the formation of Cu(II) and Co(II).[5] The results could be explained by a model[5] invoking a reactive charge-transfer excited state of $[Cu(dmp)_2]^+$, but direct evidence for this model, e.g., in the form of supporting emission work, has been lacking. The idea that a photoexcited state of $[Cu(dmp)_2]^+$ may survive to undergo bimolecular reactions in solution is supported by the report that the complex has been used to sensitize the fluorescence of organic dyes with low-lying singlet states.[6] However, Balzani has cautioned that the latter experiments involve important corrections for direct excitation and that few experimental details were provided.[1a] Recently, Ferraudi carried out flash photolysis studies of $[Cu(dmp)_2]^+$ and reported observing a long-lived, presumably non-excited-state species that decays by a second-order process.[7a] He originally suggested that this intermediate might be the reducing species involved in our studies, but more recent results suggest that this intermediate forms only upon UV excitation.[7b] Hence, it may not be relevant to our work.

Although we have reported observing emission from charge-transfer excited states of Cu(I) complexes, including $[Cu(dmp)_2]^+$, the results to date have been confined to low-temperature glasses or the solid state.[8] In this report we describe the first emission and emission quenching studies of $[Cu(dmp)_2]^+$ in fluid solution. In addition, the pronounced effect that the addition of Lewis bases has on the emission is also described.

Experimental Section

Materials. The preparation of $[Cu(dmp)_2]NO_3 \cdot 2.5H_2O$ and $[Cu(dmp)_2]BF_4$ followed the method used previously;[5a] recrystallization was from ethanol/water. $Co(acac)_3$ and $Cr(acac)_3$ were prepared according to literature methods, recrystallized from methylene chloride/toluene, and sublimed under vacuum prior to use. All other materials were reagent grade quality. The solvent methylene chloride was obtained from Burdick and Jackson Laboratories, Inc. (distilled in glass grade), and was deoxygenated by an Ar stream or by repeated freeze/pump/thaw cycles.

Apparatus. The lifetime was measured from a standard log plot of data obtained with a N_2 laser system that has previously been described.[9] Absorption measurements were made with a McPherson EU-707D spectrophotometer or with a Cary 17D spectrophotometer. The quantum yield and most of the quenching measurements were made by using a Perkin-Elmer MPF 44B fluorescence spectrophotometer with the cell holder thermostated at 25 °C using a Tri-R Instruments Model B-30 circulating water bath. Some of the early fluorescence measurements were carried out on a SPEX Fluorolog instrument.

Methods. The emission spectra of $\sim 3 \times 10^{-5}$ M solutions of $[Cu(dmp)_2]BF_4$ in deoxygenated CH_2Cl_2 were excited at 454 nm. The emission intensities at 670 nm were used in the analyses of the quenching studies. Most of the quenchers used did not absorb at 454 or 670 nm, but absorption corrections[10] were necessary for the measurements involving $Cr(acac)_3$ and $Co(acac)_3$. Linear Stern-Volmer plots[11] were obtained for all quenchers.

The luminescence quantum yield of $[Cu(dmp)_2]^+$ at 25 °C was measured relative to an aqueous solution of $[Ru(bpy)_3]^{2+}$ (ϕ 0.042 ± 0.003[12]), correcting for changes in the refractive index.[13] The optical densities of the sample and the standard solutions were carefully matched prior to the measurements. The emission spectra were corrected by the method of Lippert.[14]

Results

The absorption and corrected emission spectra of $[Cu(dmp)_2]^+$ in CH_2Cl_2 at 25 °C are shown in Figure 1. The absorption maximum is at 454 nm (ϵ 7950 M^{-1} cm^{-1}); the corrected emission maximum is at 730 nm. The emission is extremely weak or undetectable at room temperature with water, ethanol, methanol, acetonitrile, or acetone as a solvent, but emission is observed in $CHCl_3$. The emission lifetime is 54 ± 10 ns, and the quantum yield of emission is $\sim 2 \times 10^{-4}$.

---

(1) (a) Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321. (b) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.

(2) (a) Kirch, M.; Lehn, J. M.; Sauvage, J. *Helv. Chim. Acta* **1979**, *62*, 1345. (b) Brown, G. M.; Brunschwig, B. S.; Creutz, C.; Endicott, J. F.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 1298. (c) DeLaive, P. J.; Sullivan, B. P.; Meyer, T. J.; Whitten, D. G. *Ibid.* **1979**, *101*, 4007. (d) Gray, H. B.; Mann, K. R.; Lewis, N. S.; Thich, J. A.; Richman, R. M. *Adv. Chem. Ser.* **1978**, *No. 168*, 44.

(3) Balzani, V.; Bolletta, F.; Scandola, F.; Ballardini, R. *Pure Appl. Chem.* **1979**, *51*, 299.

(4) Adamson, A. W. *Pure Appl. Chem.* **1979**, *51*, 313.

(5) (a) McMillin, D. R.; Buckner, M. T.; Ahn, B. T. *Inorg. Chem.* **1977**, *16*, 943. (b) Ahn, B. T.; McMillin, D. R. *Ibid.* **1978**, *17*, 2253.

(6) Wehry, E. L.; Sundararajan, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1135.

(7) (a) Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 1370. (b) Ferraudi, G., private communication.

(8) (a) Buckner, M. T.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1978**, 759. (b) Buckner, M. T.; Matthews, T. G.; Lytle, F. E.; McMillin, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 5846. (c) Blasse, G.; McMillin, D. R. *Chem. Phys. Lett.* **1978**, *70*, 1.

(9) Watts, R. J.; Brown, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 6029

(10) Demas, J.; Adamson, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 5159.

(11) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park Calif., 1978; pp 247-248.

(12) Van Houten, J.; Watts, R. J. *J. Am Chem. Soc.* **1975**, *97*, 3843.

(13) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, *85*, 587.

(14) Lippert, E.; Nägele, W.; Seibolt-Blankenstein, I.; Staiger, U.; Voss, W. *Fresenius' Z. Anal. Chem.* **1959**, *170*, 1.

0020-1669/80/1319-3519$01.00/0

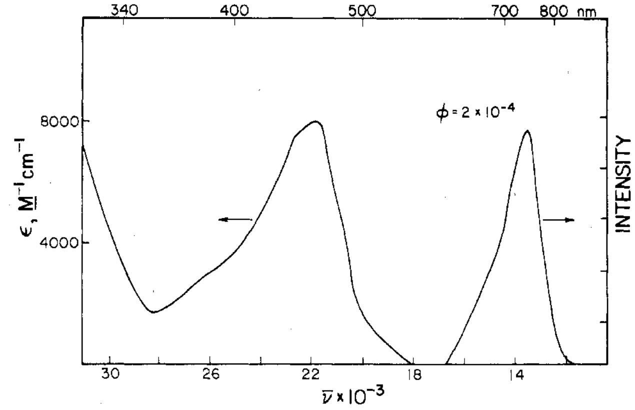


Figure 1. Visible absorption and corrected emission spectra of $[Cu(dmp)_2]^+$ in CH_2Cl_2 at 25 °C.

Table I. Quenching Results with the Nitrobenzene Derivatives

quencher	k_q, $M^{-1}\,s^{-1}$	K_{sv}, M^{-1}	$-E_{1/2}$ vs. SCE,[a] V
m-dinitrobenzene	5.5×10^9	300.0	0.898[b]
nitrobenzene	1.8×10^9	96.6	1.147[b]
p-nitrotoluene	1.4×10^9	80.0	1.22[b]
p-nitroanisole	2.3×10^9	125.0	1.26[c]
p-nitroaniline	2.1×10^9	115.0	1.38[c]
hexachlorobenzene	$<10^9$	<50	1.44[c]
o-chlorobenzonitrile	$<10^9$	<50	1.80[d]

[a] Measured in acetonitrile or methylene chloride containing 0.1 M tetra-*n*-propylammonium perchlorate. [b] Maki, A. H.; Geske, D. H. *J. Am. Chem. Soc.* **1961,** *83,* 1952. [c] Roy, J. K.; Carroll, F. A.; Whitten, D. G. *Ibid.* **1974,** *96,* 6349. [d] Measured in DMF containing 0.1 M tetraethylammonium perchlorate: Bartak, D.; Houser, K.; Rudy, B.; Hawley, M. *Ibid.* **1972,** *94,* 7526.

(The estimate of the quantum yield is the correct order of magnitude but could be in error by as much as a factor of 2. The major source of error stems from the severe corrections required to obtain emission spectra which are undistorted by the detector response.[14])

When solutions of $[Cu(dmp)_2]^+$ and the various quenchers are kept in the dark at room temperature, the absorbance is stable for long periods of time. Also, during the emission studies, after the solutions had been exposed to the 454-nm light, no change in the absorbance was noted. And no new absorption features were observed in solutions which contained both $[Cu(dmp)_2]^+$ and quenchers.

Several standard electron-transfer quenchers were used in this study, and the results obtained are compiled in Table I, where, for ease of reference, we have listed the quencher reduction potentials as well as the quenching rate constants, calculated from eq 1b. In these equations P° is the emission

$$\frac{P^\circ}{P} - 1 = K_{sv}[Q] \tag{1a}$$

$$K_{sv} = k_q\tau \tag{1b}$$

intensity without quencher, P is the emission intensity when the quencher concentration is [Q], K_{sv} is the Stern–Volmer constant, k_q is the second-order rate constant associated with the quenching event, and τ is the excited-state lifetime. The K_{sv}'s were obtained from least-squares plots of the emission intensities as a function of [Q] with use of eq 1a. *Apparent* Stern–Volmer constants obtained for other systems are listed in Table II, and representative plots are presented in Figure 2.

Discussion

The excitation spectrum of the emission exhibits a maximum at the MLCT band of $[Cu(dmp)_2]^+$ and is attributed to an excited state of the complex which will provisionally be designated by $*[Cu(dmp)_2]^+$. (At this point we could only speculate as to what extent the complex may undergo specific solvation interaction or be involved in ion pair formation with the anion, etc.) Since the spin multiplicity is expected to be a useful label for the electronic states of complexes of first-row transition metals, the low-lying excited states of $[Cu(dmp)_2]^+$ may be designated as $^1d{-}\pi^*$ and $^3d{-}\pi^*$ charge-transfer states. In principle, the emission could occur from either of these, or it could reflect a thermal average of the two.[15] For the purpose of obtaining a "feel" for the magnitude of τ_{rad}, the radiative lifetime of the emission, we assume that a single emitting level is involved and calculate that

Table II. Apparent Stern–Volmer Constants for the Lewis Bases and the Metal Complexes

quencher	K_{sv}, M^{-1}	quencher	K_{sv}, M^{-1}
acetonitrile	1.56	$Co(acac)_3$[a]	73.17
methanol	0.68	$Cr(acac)_3$[a,b]	6.72
ethanol	1.10		

[a] The ligand is acetylacetonate. [b] The absorption corrections are severe for this system, and the K_{sv} value is therefore less certain.

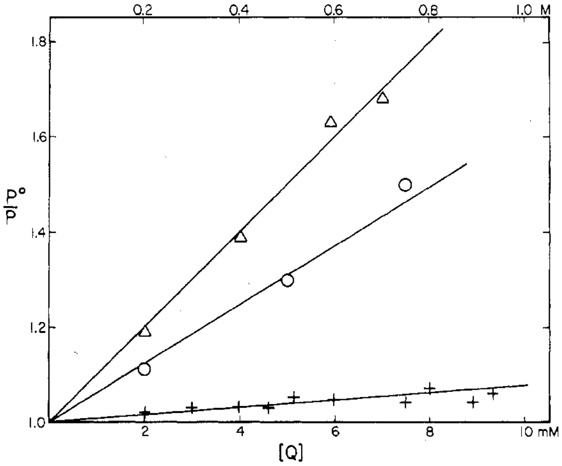


Figure 2. Stern–Volmer plots describing the effect of nitrobenzene (△), methanol (○), and $Cr(acac)_3$ (+) on the emission of $*[Cu(dmp)_2]^+$. The abscissa is calibrated in mM units for nitrobenzene and $Cr(acac)_3$ and in M units for methanol.

$$\tau_{rad} \approx \tau/\phi = 270\ \mu s \tag{2}$$

A τ_{rad} of this magnitude would be associated with a state having significant triplet character.[16] The $^3d{-}\pi^*$ state may be directly involved in the emission process or indirectly if the emission is delayed fluorescence via the $^1d{-}\pi^*$ level. Consistent with this reasoning, from related Cu(I) systems we have observed considerably shorter lived emission ($\tau \lesssim 1$ ns at 90 K) which we have suggested is probably prompt emission from $^1d{-}\pi^*$ levels.[8a,b] Incidentally, the fact that the emission decays by an apparent first-order process implies that we can rule out the possibility of recombination delayed emission which might have occurred if the complex dissociated into radicals upon excitation. (See ref 7a.)

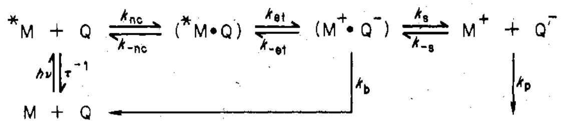
In our first series of quenching studies we have used a series of substituted nitrobenzene derivatives as substrates because (1) their reduction potentials are such that thermal electron transfer is not important, (2) the molecules are characterized by relatively high triplet energies (e.g., 2.1 μm^{-1} for nitro-

---

(15) Crosby, G. A. *Acc. Chem. Res.* **1975,** *8,* 231.

(16) Porter, G. B. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 2.

Scheme I



benzene[17]), and therefore energy-transfer quenching is not expected, and (3) their reduction potentials are in the range of that anticipated for the $[Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+$ couple, vide infra, and therefore electron-transfer quenching is expected. In the line with the Rehm and Weller model[18] the results can be discussed by using Scheme I. The species (*M·Q) and $(M^+ \cdot Q^-)$ denote encounter complexes, M is the copper(I) complex, Q is the quencher, and τ is the lifetime of photoexcited $[Cu(dmp)_2]^+$. Since no net photochemistry was detected, the k_p step is neglected, and with the usual steady-state approximations, the observed quenching constant is obtained by eq 3.

$$k_q^{obsd} = \frac{k_{nc}}{1 + \dfrac{k_{-nc}}{k_{et}} + \dfrac{k_{-nc}k_{-et}}{k_b k_{et}}} \qquad (3)$$

With the assumption that $\Delta G^{\ddagger}$, the activation free energy of an electron-transfer reaction, can be expressed as a function of the free energy of reaction and a reorganizational energy λ characteristic of the reagents involved, the equation for k_q^{obsd} can be expressed as a function of k_{nc}, k_{-nc}, ΔG_{et} (the free energy of the reduction of Q by *M), ΔG_b (the free energy of the reduction of M^+ by Q^-), Z (a collision frequency), and λ.[3,18] If $k_b = Z \exp(-\Delta G_b^{\ddagger}/RT)$ is approximated as Z[3,19]

$$k_q^{obsd} = \frac{k_{nc}}{1 + \dfrac{k_{-nc}}{Z}[\exp(\Delta G_{et}^{\ddagger}/RT) + \exp(\Delta G_{et}/RT)]} \qquad (4a)$$

where according to Weller's model[18]

$$\Delta G_{et}^{\ddagger} = \frac{\Delta G_{et}}{2} + \left[\left(\frac{\Delta G_{et}}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2\right]^{1/2} \qquad (4b)$$

Finally, ΔG_{et} can be written in terms of the reduction potentials of the species involved and W_p and W_r, which are, respectively, the work terms required to bring the product ions and reactions together expressed in electronvolts (eq 5). For

$$\Delta G_{et} = E_{1/2}([Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+) - E_{1/2}(Q/Q^-) + W_p - W_r \qquad (5)$$

a closely related series of quenchers k_{nc}, k_{-nc}, Z, λ, and the work terms can be assumed to be constant. Thus the equations predict that quenching will occur at or near the diffusional limit for quenchers with a favorable ΔG_{et} and that k_q^{obsd} will drop off as $E_{1/2}(Q/Q^-)$ becomes negative with respect to $E_{1/2}([Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+)$, and in several cases this type of behavior has been observed.[3] Therefore from the results in Table I we estimate that

$$E_{1/2}([Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+) \lesssim -1.4 \text{ V vs. SCE} \qquad (6)$$

Alternatively, $E_{1/2}([Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+)$ can be crudely estimated from spectral data. Since the energy difference between the lowest singlet and triplet charge-transfer states will be small,[8b,15] we can approximate the zero–zero energy of the reactive excited state by half the sum of the energies of the absorption and emission maxima (2.2 V). If we further assume that the entropy content of $[Cu(dmp)_2]^+$ and $*[Cu(dmp)_2]^+$ are the same, then

$$E_{1/2}([Cu(dmp)_2]^{2+}/*[Cu(dmp)_2]^+) \approx E_{1/2}([Cu(dmp)_2]^{2+}/[Cu(dmp)_2]^+) - 2.2 \text{ V} \qquad (7)$$

Since the ground-state potential is ~0.4 V,[20] we calculate that the Cu(II)/Cu(I) potential is around −1.8 V when $*[Cu(dmp)_2]^+$ is involved. Given the approximations and uncertainties involved, the agreement between the "experimental" value and the calculated value is reasonable, and by any account it is evident that $*[Cu(dmp)_2]^+$ is a potent, albeit short-lived, reductant.

Of the systems listed in Table II only $Co(acac)_3$ and perhaps $Cr(acac)_3$ could be expected to be electron-transfer quenchers. The reduction potentials for $Co(acac)_3$ and $Cr(acac)_3$ are reportedly −0.26 and −1.81 V vs. SCE, respectively.[21] Energy transfer from $*[Cu(dmp)_2]^+$ to either $Co(acac)_3$ or $Cr(acac)_3$ is probably exoergic and therefore provides an alternative to electron-transfer quenching. The energy[22] of the lowest doublet state of $Cr(acac)_3$ is ~1.28 μm^{-1} (1.6 V), and although we do not know the energy of the lowest excited state of $Co(acac)_3$, the fact that its absorption spectrum has a transition maximizing as low as 595 nm (2.1 V) suggests that excited states of $Co(acac)_3$ may well lie below that of $*[Cu(dmp)_2]^+$. Unfortunately, neither $Co(acac)_3$ nor $Cr(acac)_3$ was found to exhibit detectable luminescence in CH_2Cl_2 at room temperature, and we lack a direct method for establishing whether electron transfer or energy transfer occurs with these systems. Consistent with an electron-transfer mechanism, a *net* redox reaction occurs with the formation of Co(II) on irradiating solutions containing $[Cu(dmp)_2]^+$ and $Co(acac)_3$ in alcohol/water mixtures.[24] The reason a *net* reaction can be observed under these conditions probably owes to the fact that the electron-transfer products $[Cu(dmp)_2]^{2+}$ and $[Co(acac)_3]^-$ can be readily solvolyzed in the alcohol/water medium, thereby providing a k_p step which is competitive with the k_b step in Scheme I. It might also be argued, that, since quenching with $Co(acac)_3$ is essentially diffusion controlled ($k_q^{obsd} = 1.9 \times 10^9$ M^{-1} s^{-1}), electron-transfer quenching is the more likely mechanism. This is because a collisional mechanism for energy transfer usually is obtained when d–d states are involved due to their low dipole strength, and the ligands around the Co(III) center are likely to hinder the contact between the d orbitals of cobalt and orbitals of $*[Cu(dmp)_2]^+$.[23] If so, the rate of energy-transfer quenching would be expected to be significantly below the diffusion limit. On the other hand, the quenching rate constant for $Cr(acac)_3$ (~1×10^8 M^{-1} s^{-1}) is probably reasonable for energy transfer, although it could be argued that the mechanism involves electron transfer but that ΔG_{et} is less favorable.

The other systems listed in Table II are rather novel in that they are unlikely candidates for (electronic) energy transfer *or* for electron-transfer quenching. However, *any interaction* that alters the electronic and vibrational energy level schemes of the system will affect the radiative and nonradiative processes of the system and therefore can affect the emission. Elucidating how these systems operate must await further

---

[17] Lewis, G. N.; Kasha, M. *J. Am. Chem. Soc.* **1944**, *66*, 2100.

[18] (a) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[19] Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993.

[20] (a) Thomas, P.; Spindler, H.; Rehorek, D.; Gurtler, O. *Z. Chem.* **1973**, *13*, 225. (b) Patterson, G. S.; Holm R. H. *Bioinorg. Chem.* **1975**, *4*, 257.

[21] Murray, R. W.; Hiller, L. K. *Anal. Chem.* **1967**, *39*, 1221.

[22] Schlafer, H. L.; Gausmann, H.; Witzke, H. *J. Chem. Phys.* **1967**, *46*, 1423.

[23] Porter, G.; Wright, M. R. *Discuss. Faraday Soc.* **1959**, *27*, 7. (b) Balzani, V.; Indelli, M. T.; Maestri, M.; Sandrini, D.; Scandola, F. *J. Phys. Chem.* **1980**, *81*, 582.

[24] Ahn, B. T.; McMillin, D. R., unpublished results.

experimentation; nevertheless, two of the more straightforward mechanistic possibilities can be briefly considered The first involves covalent solvation[25] of the coordinated dmp ligands. Such solvation has, for example, been proposed to rationalize the solution photophysics of bipyridine.[26] (But see also ref 27.) If covalent solvation has any significance for the ligands of $*[Cu(dmp)_2]^+$, however, it probably cannot explain the results for all quenchers, since the interaction seems improbable for acetonitrile.

A second phenomenon—coordination at the metal center—is an intriguing alternative. One obvious property that the alcohols and acetonitrile have in common is their Lewis basicity. Since the metal center is formally Cu(II) in the d–π^* excited state, the addition of a fifth donor group about the metal is possible. In fact it has been proposed[28] that solvent and/or counterions do associate with the (ground state) Cu(II) analogue $[Cu(dmp)_2]^{2+}$. Moreover, coordination numbers of 5 and 6 are well established for related phenanthroline[29] and bipyridine complexes[30] of Cu(II). That an excited state may be capable of exhibiting an expanded coordination number has previously been suggested in the case of certain Cr(III) systems.[31] In addition, in a recent structural report it was noted that the Cr(III) center in the bis(terpyridyl) complex is rather exposed, and it was suggested that solvent interactions with the metal center may be responsible for the short excited-state lifetime of the complex.[32]

Conclusions

Strong evidence for a reactive charge-transfer excited state of $[Cu(dmp)_2]^+$ has been obtained from emission quenching studies in CH_2Cl_2. The excited state is strongly reducing, and most of the excited state energy seems to be available as electrochemical potential. Donor solvents appear to quench the emission, possibly by interaction at the metal center. CH_2Cl_2 may be a good solvent for use in photostudies of complexes exhibiting relatively "exposed" metal centers; however, it should be emphasized that CH_2Cl_2 can undergo reaction with excited molecules[33] and can influence the reactivity of excited molecules.[34]

Acknowledgment. The authors gratefully acknowledge the Atlantic Richfield Foundation which has helped fund our work through a contribution to the Research Corp. They also thank Richard J. Watts, who provided the lifetime measurement and a corrected emission spectrum of $[Ru(bpy)_3]^{2+}$.

Registry No. $[Cu(dmp)_2]^+$, 21710-12-3.

---

(25) Gillard, R. D. *Coord. Chem. Rev.* **1975**, *16*, 67.
(26) Henry, M. S.; Hoffman, M. Z. *J. Phys. Chem.* **1979**, *83*, 618.
(27) Kotlicka, J.; Grabowski, Z. R. *J. Photochem.* **1979**, *11*, 413.
(28) (a) Hall, J. R.; Marchant, N. K.; Plowman, R. A. *Aust J. Chem.* **1963**, *16*, 34. (b) Rehorek, D. *Z. Chem.* **1978**, *18*, 32. (c) Sundararajan, S.; Wehry, E. L. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3699.
(29) (a) Nakai, H.; Noda, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1386. (b) Anderson, O. P. *Inorg. Chem.* **1975**, *14*, 730.
(30) (a) Barklay, G. A.; Hoskins, B. F.; Kennard, C. H. L. *J. Chem. Soc.* **1963**, 5691. (b) Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1350. (c) Proctor, J. M.; Stephens, F. S. *J. Chem. Soc. A* **1969**, 1248.
(31) (a) Sandrini, D.; Gandolfi, M. T.; Juris, A.; Balzani, V. *J. Am. Chem. Soc.* **1977**, *99*, 4523. (b) Jamieson, M. A.; Serpone, N.; Henry, M. S.; Hoffman, M. Z. *Inorg. Chem.* **1979**, *18*, 214.
(32) Wickramasinghe, W. A.; Bird, P. H.; Jamieson, M. A.; Serpone, N. *J. Chem. Soc., Chem. Commun.* **1979**, 798.
(33) (a) Saperstein, D.; Levin, E. *J. Chem. Phys.* **1979**, *62*, 3560. (b) Felt, G. R.; Linke, S.; Lwowski, W. *Tetrahedron Lett.* **1972**, 2037.
(34) (a) Gleria, M.; Minto, F.; Beggiato, G.; Bortolus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 285. (b) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860.

Contribution from the Christopher Ingold Laboratories,
University College, London WC1H OAJ, United Kingdom

Electronic and Resonance Raman Spectra of Mixed-Valence Linear-Chain Complexes of Platinum with 1,3-Diaminopropane

ROBIN J. H. CLARK* and MOHAMEDALLY KURMOO

Received February 29, 1980

The resonance Raman spectra of mixed-valence complexes $[Pt(tn)_2][Pt(tn)_2X_2]Y_4$ (tn = 1,3-diaminopropane, X = Cl, Br, or I for Y = ClO_4, and X = Br for Y = BF_4) have been recorded at ca. 80 K by use of excitation lines whose wavenumbers fall within the contours of the intense, axially polarized intervalence bands of each complex. The resonance Raman and specular reflectance spectra of a single crystal of $[Pt(tn)_2][Pt(tn)_2Br_2](ClO_4)_4$ have also been recorded, at room temperature. The resonance Raman spectra are characterized by the appearance of an intense progression $v_1\nu_1$, where ν_1 is the symmetric (X–Pt^{IV}–X) stretching mode. The maximum value of v_1 ranges from 4 to 18. Other short progressions, $\nu_n + v_1\nu_1$, based on other Raman-active modes, have also been observed. From the observed progressions the spectroscopic constants ω_1 and x_{11} have been calculated. The specular reflectance and polarized Raman spectra from single crystals show semiconductor behavior in one direction. The excitation profiles of ν_1 (both Stokes and anti-Stokes bands), $2\nu_1$ (Stokes bands), and (in some cases) $3\nu_1$ (Stokes bands) all maximize within 500 cm^{-1} of each other, and all on the low wavenumber side of the resonant mixed-valence band in each case.

Introduction

Previous studies in this series on mixed-valence complexes of platinum and palladium, belonging to Class II in the Robin and Day[1] scheme, have been focused on complexes containing ethylamine,[2-4] ammonia,[5] 1,2-diaminopropane,[6] and 1,2-diaminoethane.[7] The present paper develops this subject further and is concerned with platinum complexes with 1,3-diaminopropane (tn), $[Pt(tn)_2][Pt(tn)_2X_2]Y_4$ (X = Cl, Br, or I for Y = ClO_4 and X = Br for Y = BF_4). This ligand, which forms a six-membered aliphatic ring with the metal atom, appears to form linear-chain complexes with as much facility as is found for monodentate amines and for other bidentate amines capable of forming five-membered aliphatic rings with the metal atom. The results obtained add substantially to the body

---

(1) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1968**, *10*, 247.
(2) Clark, R. J. H.; Franks, M. L.; Trumble, W. R. *Chem. Phys. Lett.* **1976**, *41*, 287.
(3) Clark, R. J. H.; Franks, M. L. *J. Chem. Soc., Dalton Trans.* **1977**, 198.
(4) Clark, R. J. H.; Turtle, P. C. *Inorg. Chem.* **1978**, *17*, 2526.
(5) Clark, R. J. H.; Turtle, P. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1622.
(6) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1.
(7) Campbell, J. R.; Clark, R. J. H.; Turtle, P. C. *Inorg. Chem.* **1978**, *17*, 3623.