

Reductive Quenching of Photoexcited $\text{Cu}(\text{dipp})_2^+$ and $\text{Cu}(\text{tptap})_2^+$ by Ferrocenes (dipp = 2,9-Diisopropyl-1,10-phenanthroline and tptap = 2,3,6,7-Tetraphenyl-1,4,5,8-tetraazaphenanthrene)

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The metal-to-ligand charge-transfer excited states of $\text{Cu}(\text{NN})_2^+$ systems tend to be good reducing agents but poor oxidants for kinetic and thermodynamic reasons. However, this report demonstrates that reductive electron-transfer quenching is an important pathway for ferrocenes that react with the photoexcited states of $\text{Cu}(\text{dipp})_2^+$ and $\text{Cu}(\text{tptap})_2^+$ in methylene chloride (dipp = 2,9-diisopropyl-1,10-phenanthroline and tptap = 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenanthrene). In the case of the dipp complex the bulky isopropyl substituents inhibit structural relaxation within the excited state, and the self-exchange rate for reductive quenching is quite favorable, $k_{**} \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. Even in the absence of a significant kinetic barrier to reaction, however, for energetic reasons only extensively methylated ferrocene derivatives with relatively negative reduction potentials are capable of transferring an electron to the excited state. In contrast, every ferrocene derivative investigated, except diacetyl ferrocene, reacts with the charge-transfer excited state of the tptap complex by an electron-transfer mechanism. This is mainly due to a difference in driving force which is about 0.5 V greater for the tptap complex. This system also has a favorable self-exchange rate, $k_{**} \approx 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, evidently because the juxtapositioned phenyl substituents inhibit low-symmetry distortions within the ground state as well as the excited state. Although energy transfer to ferrocene is also possible, this is a less competitive process with the tptap complex because the zero-zero energy of the reactive excited state is rather low (${}^3E_{00} \approx 1.7 \text{ V}$).

Introduction

Complexes of low-valent metal centers such as copper(I) or ruthenium(II) with π -accepting, heteroaromatic chelating ligands such as 1,10-phenanthroline tend to exhibit strong visible absorption bands. (In the following NN is the designation for a ligand of this type.) The strongly allowed excitations involve metal-to-ligand charge-transfer (CT) excited states which, from the point of view of reactivity, are both better oxidizing and better reducing agents than their ground-state precursors.^{1–4} Regarding $\text{Cu}(\text{NN})_2^+$ systems, several studies have shown that the photoexcited states are potent reducing agents,^{5–8} in some cases reactive enough to induce the reductive cleavage of benzylic carbon–halogen bonds.⁷ However, initial attempts to

utilize the copper systems as photooxidants failed.^{9,10} If $E_0^{+/0}$ represents the electrode potential of the ground-state couple, then $*E_0^{+/0}$, the corresponding potential for the reduction of the excited state ($*\text{Cu}(\text{NN})_2^+ + e^- = \text{Cu}(\text{NN})_2^0$), is more positive by E_{00} , the separation (in volts) between the zero-point energies of the two electronic states.¹ Even though the excited state is more oxidizing, electron transfer from quencher Q is still likely to be an uphill process if E_{00} is modest and $E_0^{+/0}$ is relatively negative as is usually the situation with $\text{Cu}(\text{NN})_2^+$ systems. The discussion will show that kinetic constraints may exist as well.

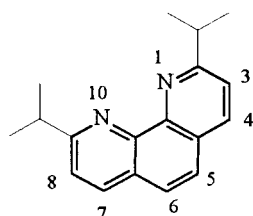
Despite these limitations, recent work has shown that reductive quenching of the CT states is possible. In particular, studies involving a series of methylated ferrocenes as quenchers of photoexcited $\text{Cu}(\text{dmp})_2^+$ and $\text{Cu}(\text{dpp})_2^+$ showed that energy-transfer quenching was the dominant process but that electron-transfer quenching occurred with the most reducing substrate, dexamethylferrocene¹¹ (dmp denotes 2,9-dimethyl-1,10-phenanthroline and dpp denotes 2,9-diphenyl-1,10-phenanthroline). Ferrocenes are useful reagents because they are soluble in weakly polar media like CH_2Cl_2 , and the potentials occur in a convenient range. In an effort to develop better photooxidants, the focus of the present investigation is on the $\text{Cu}(\text{dipp})_2^+$ and $\text{Cu}(\text{tptap})_2^+$ systems, where dipp and tptap denote the 2,9-diisopropyl-1,10-phenanthroline and 2,3,6,7-tetraphenyl-1,4,5,8-tetraazaphenanthrene ligands, respectively. The results show that the presence of isopropyl substituents minimizes the kinetic

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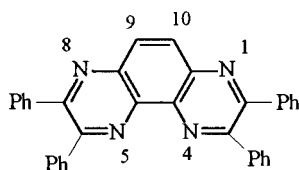
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- (1) Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
- (2) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1–64.
- (3) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992; Chapter 6, pp 105–212.
- (4) Horváth, O.; Stevenson, K. L. *Charge-Transfer Photochemistry of Coordination Compounds*; VCH Publishers: New York, 1993; Chapter 3, pp 21–32.
- (5) McMillin, D. R.; Kirchoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83–92.
- (6) Gamache, R. E., Jr.; Rader, R. A.; McMillin, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 1141–1146.
- (7) Kern, J. M.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1987**, 546–548.
- (8) Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* **1996**, *35*, 6406–6412.

- (9) Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Inorg. Chem.* **1989**, *28*, 4070–4072.
- (10) Karlsson, K.; Moucheron, C.; Kirsch-DeMesmaeker, A. *New J. Chem.* **1994**, *18*, 721–729.
- (11) Cunningham, K. L.; Hecker, C. R.; McMillin, D. R. *Inorg. Chim. Acta* **1996**, *242*, 143–147.



2,9-diisopropyl-1,10-phenanthroline

2,3,6,7-tetraphenyl-
1,4,5,8-tetraazaphenanthrene

problems, but the thermodynamics of reductive quenching are still unfavorable. However, in the case of the tptap complex, first introduced by Karlsson et al.,¹⁰ the reduction potential is much more favorable, and electron-transfer quenching proves to be an efficient process. Moreover, the inner-sphere reorganizational energy requirement is rather modest; the main limitation is the relatively short excited state lifetime.

Experimental Section

Materials. Aldrich Chemical Co. was the vendor for most of the reagents used including 1,10-phenanthroline, 4-nitro-1,2-phenylenediamine, isopropyl chloride, benzil, acetyl chloride, anhydrous aluminum trichloride, 4-nitroaniline, ferrocene (FeCp_2), decamethylferrocene (FeCp_2^*), lithium cyclopentadiene (LiCp), and lithium 1,2,3,4-tetra-methylcyclopentadienide (LiMe_4Cp). They also supplied *n*-butyllithium ($n\text{BuLi}$) and NaCp^* as 2.0 M solutions in hexane and THF, respectively, as well as the electrolyte tetrabutylammonium hexafluorophosphate (TBAH). Strem Chemical Company supplied dimethylferrocene ($\text{Fe}(\text{MeCp})_2$) and anhydrous FeCl_2 . The B&J labeled solvents acetonitrile and methylene chloride came from Baxter Scientific. The laser dyes, Coumarin 480 and Rhodamine 590, were from Exciton.

Methods. A slight modification of a literature procedure yielded the salt $[\text{Cu}(\text{dpp})_2]\text{TFPB}$, where TFPB^- designates the counterion tetrakis[3,5-bis(trifluoromethyl)phenyl] borate.¹² The same method yielded $[\text{Cu}(\text{tptap})_2]\text{TFPB}$ and $[\text{Cu}(\text{dipp})_2]\text{TFPB}$ in conjunction with the ligands tptap^{10,13} and dipp. The ^1H NMR (CDCl_3) spectrum of $[\text{Cu}(\text{tptap})_2]\text{TFPB}$ contained precisely those peaks reported for the BF_4^- salt¹³ as well as signals at δ 7.7 (m) and δ 7.4 (s) due to TFPB^- . The preparation of dipp followed the method of Pallenberg et al.¹⁴ Microanalysis of $[\text{Cu}(\text{dipp})_2]\text{TFPB}$. Calcd: C, 56.12; H, 3.60; N, 3.85. Found: C, 55.99; H, 3.60; N, 3.74. ^1H NMR (CDCl_3): δ 8.14 (2H, d), 7.68 (2H, s), 7.54 (2H, d), 3.55 (1H, sep) and 1.45 (12H, d). Application of literature methods yielded pentamethylferrocene, FeCpCp^* ,¹⁵ octamethylferrocene, $\text{Fe}(\text{CpMe}_4)_2$,¹⁶ and *p*-nitrophenylferrocene, $\text{FeCp}(\text{CpPhNO}_2)$,¹⁷ as well as mono- and 1,1'-diacetylferrocene, or $\text{FeCp}(\text{CpAc})$ and $\text{Fe}(\text{CpAc})_2$, respectively.¹⁸ The preparation of $\text{Na}[\text{TFPB}]\cdot x\text{H}_2\text{O}$ followed the procedure published by Nishida et al.¹⁹

Table 1. Electrochemical Data for Copper Complexes at Room Temperature

complex	solvent	E_0^a , V vs $\text{Fc}^{+/0}$	
		$\text{Cu}(\text{NN})_2^{2+/+}$	$\text{Cu}(\text{NN})_2^{+/0}$
$\text{Cu}(\text{tptap})_2^+$	CH_2Cl_2	0.93 (70)	-1.51 (60)
	CH_3CN	0.77 ^b	-1.43 ^b
$\text{Cu}(\text{dipp})_2^+$	CH_2Cl_2	0.59 (80)	
	CH_3CN	0.49 (60)	-2.21 (50)
$\text{Cu}(\text{dpp})_2^+$	CH_2Cl_2	0.37 (70)	
	CH_3CN	0.29 (50)	-2.10 (60)
$\text{Cu}(\text{dmp})_2^+$	CH_2Cl_2	0.28 ^c	-2.09 ^c
	CH_3CN	0.50 (80)	
	CH_2Cl_2	0.27 (75)	-2.18 (50)
	CH_3CN		

^a Electrolyte is 0.1 M TBAP. $\text{Fc}^{+/0}$ denotes the potential for ferrocene. The numbers in parentheses are the peak-to-peak separations in mV. ^b From ref 10. Shift to $\text{Fc}^{+/0}$ reference obtained from data reported for the $\text{Cu}(\text{dmp})_2^+$ system. ^c Federlin, P.; Kern, J. M.; Rastegar, A.; Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *New J. Chem.* **1990**, 14, 9–12. Calibration to $\text{Fc}^{+/0}$ as above.

The solvent for all luminescent measurements was methylene chloride, and the temperature was ambient. The deoxygenation procedure involved a series of freeze-pump-thaw cycles. In the fluorometer studies the excitation wavelength was usually 480 nm, while 600 and 625 nm long-wave-pass filters blocked spurious light from reaching the detector. Due to the strong absorption of monoacetyl- and 1,1'-diacetylferrocene at 480 nm, the excitation wavelength was at 590 nm with these quenchers. A user-written program TAU.RES successfully fit the decay data to an exponential form. In all cases, the residual plots justified the use of a single exponential. Stern-Volmer plots of the rate constants for luminescence decay versus the concentration of quencher yielded estimates of the quenching constants.²⁰ The method of Parker and Rees²¹ proved useful for estimating the relative emission yields. An earlier publication describes the method used to correct the emission spectra.²²

For the cyclic voltammetry measurements, the working electrode was a gold disk, and a platinum wire served as the auxiliary electrode. The reference was a AgCl/Ag electrode containing 3 M NaCl. For reporting purposes the reference is the ferrocenium/ferrocene ($\text{Fc}^{+/0}$) couple in the same solvent medium. For comparison's sake the ferrocene couple gave a wave at 0.52 V vs AgCl/Ag in methylene chloride containing 0.1 M TBAP. The scan rate was typically 50 mV s^{-1} . Adsorption effects may influence the waveforms observed because the peak-to-peak separations of some systems decrease at higher scan rates.

Instrumentation. A BAS CV-27 cyclic voltammograph interfaced to a Hewlett-Packard 7015B X-Y recorder provided the voltammetry data. A Gemini 200 MHz FT-NMR spectrometer recorded the ^1H NMR spectra of the ligands, and a Perkin-Elmer Lambda 4C spectrophotometer yielded absorbance data. The luminescence instrument was an SLM Aminco SPF 500C. An Oxford Instruments DN1704 cryostat facilitated the low-temperature measurements. For lifetime studies, the excitation source was a Laser Science VSL-337ND-S pulsed nitrogen laser with a DLMS-220 pumped dye attachment. A Hamamatsu R928 phototube powered by a Pacific Instruments model 227 high-voltage supply monitored the emission decay. A Tektronix 520 digitizing oscilloscope captured the signal. Tektronix supplied the TEKDIG software that directed data transfer to a personal computer.

Results

Electrochemistry. Several trends are evident in the measured electrode potentials for the relevant copper complexes (Table 1). Thus, a comparison of the potentials for the tptap and dpp complexes reveals that the introduction of additional nitrogen

(12) Everly, R. M.; McMillin, D. R. *J. Phys. Chem.* **1991**, 95, 9071–9075.

(13) Moucheron, C.; Karlsson, K.; Verhoeven, C.; Nasielski-Hinkens, R. *Tetrahedron Lett.* **1993**, 34, 1163–1166.

(14) Pallenberg, A. J.; Koenig, K. S.; Barnhart, D. M. *Inorg. Chem.* **1995**, 34, 2833–2840.

(15) Cunningham, K. L.; McMillin, D. R. *Polyhedron* **1996**, 15, 1673–1675.

(16) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, 8, 287–297.

(17) Weinmayr, V. J. *J. Am. Chem. Soc.* **1955**, 77, 3012–3014.

(18) Bozak, R. E. *J. Chem. Educ.* **1966**, 43, 73.

(19) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, 57, 2600–2604.

(20) Turro, N. J. *Molecular Photochemistry*; Benjamin: Reading, MA, 1965; pp 92–93.

(21) Parker, C. A.; Rees, W. T. *Analyst (London)* **1960**, 85, 857–600.

(22) Eggleston, M. K.; McMillin, D. R.; Koenig, K. S.; Pallenberg, A. J. *Inorg. Chem.* **1997**, 36, 172–176.

Table 2. E_0 Data for Ferrocenes in CH_2Cl_2

couple	E_0 , V vs $\text{Fc}^{+/0}$	couple	E_0 , V vs $\text{Fc}^{+/0}$
$\text{Fe}(\text{CpAc})_2^{+/0}$	0.52	$\text{Fe}(\text{CpMe})_2^{+/0}$	-0.10
	0.49 ^a		
$\text{FeCp}(\text{CpAc})^{+/0}$	0.26	$\text{FeCpCp}^{*+/0}$	-0.29
	0.27 ^a		
$\text{FeCp}(\text{CpPhNO}_2)^{+/0}$	0.14	$\text{Fe}(\text{CpMe}_4)_2^{+/0}$	-0.40
$\text{FeCp}_2^{+/0}$	0.00	$\text{FeCp}_2^{*+/0}$	-0.57

^a Connelly, N. G.; Geiger, W. G. *Chem. Rev.* **1996**, *96*, 877–910.

Table 3. Physical Data from CH_2Cl_2 Solutions at Room Temperature

complex ^a	absorption		emission			$^3E_{00}$, V	$^*E_0^{+/0}$, V vs $\text{Fc}^{+/0}$
	λ , nm	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	λ_{max}^b , nm	τ , ns	ϕ_{rel}^c		
$\text{Cu}(\text{dpp})_2^{+d}$	440	3200	680	280	2.5	1.80	-0.30
	560 (sh)						
$\text{Cu}(\text{dipp})_2^{+}$	445	7500	650	365	4.0	1.95	-0.26
$\text{Cu}(\text{tptap})_2^{+}$	491		715	150	1.0	1.74	+0.23
	575 (sh)						
	490 ^e	3500 ^e	121 ^e				

^a Counterion is TFPB^- except as noted. ^b From uncorrected spectrum. ^c Relative emission quantum yield. ^d References 9 and 11. ^e Reference 10; counterion was BF_4^- .

atoms into the heteroaromatic ligand system shifts the potentials of both the metal-centered oxidation ($\text{Cu}(\text{NN})_2^{2+/+}$) and ligand-centered reduction ($\text{Cu}(\text{NN})_2^{+/0}$) processes in the positive direction. This is in line with previous results reported for ruthenium bipyridine and ruthenium bipyrazine complexes.²³ Another trend implicit in Table 1 is that an aryl-substituted phenanthroline ligand is easier to reduce than an alkyl-substituted analogue. Finally, the results support the idea that bulky alkyl substituents in the 2,9 positions of the phenanthroline favor a pseudotetrahedral coordination geometry and preferentially stabilize the copper(I) oxidation state.²² Thus, the $\text{Cu}(\text{NN})_2^{2+/+}$ potential is higher for the dipp complex than the dmp complex. The onset of the solvent limit prevents measuring the potentials for the $\text{Cu}(\text{dipp})_2^{+/0}$ and $\text{Cu}(\text{dpp})_2^{+/0}$ couples in methylene chloride. Estimated values are available from the data for acetonitrile on the assumption of a constant potential difference from the $\text{Fc}^{+/0}$ couple in both media.

Table 2 contains the potentials for the various ferrocene derivatives. As reported in the literature, the addition of each methyl substituent shifts the ferrocene potential more negative, i.e., cathodically, by about 0.05 V.^{24,25} In contrast, the addition of an electron-withdrawing substituent, such as *p*- NO_2 -phenyl or acetyl, shifts the potential in the positive direction. With the range of substituents used, the electrode potential shifts more than a volt.

Absorption and Emission Data. In addition to other information Table 3 summarizes the absorption data for the three copper complexes; plots of the spectra of the $\text{Cu}(\text{dipp})_2^{+}$ and $\text{Cu}(\text{tptap})_2^{+}$ systems are available as Supporting Information (Figure S1). As is the case with other $\text{Cu}(\text{NN})_2^{+}$ complexes,^{9,12,26} each spectrum exhibits a shoulder on the long-wavelength side of the major MLCT absorption. In the spectrum of the tptap complex the shoulder appears at around 575 nm. The intensity of the shoulder is greater for the tptap

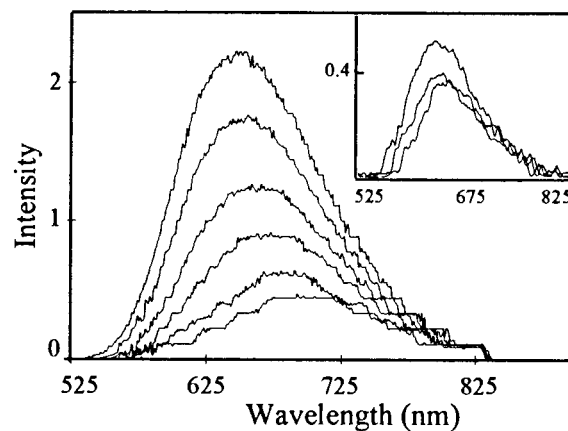


Figure 1. Uncorrected emission spectrum of $\text{Cu}(\text{dipp})_2^{+}$ at different temperatures in CH_2Cl_2 . The emission intensity decreases in the temperature order 294, 280, 260, 240, 220, and 200 K. Inset: Difference spectra between temperatures, T_1/T_2 : 280/260, 260/240, and 240/220.

than the dipp system but is not as prominent as that of the dpp complex.⁹ On the other hand, the intensity of the main CT absorbance is somewhat greater for the tptap complex as opposed to the dpp system. Although there are other factors to consider, this is at least consistent with the idea that the mesomeric interactions with the phenyl substituents may be of less consequence in the case of the tptap complex.^{27–29} Because there are two sets of cis-related phenyl substituents in the tptap system, the average orientation of each phenyl group is, in fact, likely to be approximately orthogonal to the fused-ring core.

Table 3 also contains pertinent luminescence data. The emission shifts to lower energy as the ligand ranges from dipp to dpp to tptap, and Table 3 shows that the lifetime decrease follows the same trend. As noted in Table 3, Karlsson et al. reported a shorter excited-state lifetime for $\text{Cu}(\text{tptap})_2^{+}$ in CH_2Cl_2 , but they used BF_4^- as the counterion.¹⁰ Previous work has shown that BF_4^- is capable of inducing exciplex quenching in related copper-containing systems.³⁰ As is the case with other $\text{Cu}(\text{NN})_2^{+}$ systems, the emission signals from both the dipp and the tptap systems are temperature dependent and show a decrease in intensity at lower temperatures (Figure 1). The unusual temperature dependence arises because there are two emissive excited states, and the higher energy state exhibits a significantly greater radiative rate constant.³¹ The two states involved are, in fact, singlet and triplet CT states.^{31,32} According to this model, subtraction of the emission at one temperature from the spectrum obtained at the next higher temperature yields a good approximation to the output of the higher energy ^1CT state. In line with this model, the insert in Figure 1 reveals that a series of such difference spectra parallel each other nicely. There is a slight shift to longer wavelength as the average temperature decreases, but this is probably a solvent effect. Because the excited state has a dipole moment, the emission should shift to lower energy at lower temperatures.²² At least

- (23) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617–1622.
 (24) Okuda, J.; Albach, R. W.; Herdtweck, E. *Polyhedron* **1991**, *10*, 1741–1748.
 (25) Robbins, J. L.; Edelman, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882–1893.
 (26) Parker, W. L.; Crosby, G. A. *J. Phys. Chem.* **1989**, *93*, 5692–5696.

- (27) Ichinaga, A. K.; Kirchhoff, J. R.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Inorg. Chem.* **1987**, *26*, 4290–4292.
 (28) Klemens, F. K.; Palmer, C. E. A.; Rolland, S. M.; Fanwick, P. E.; Sauvage, J. P.; McMillin, D. R. *New J. Chem.* **1990**, *14*, 129–133.
 (29) Phifer, C. C.; McMillin, D. R. *Inorg. Chem.* **1986**, *25*, 1329–1333.
 (30) Everly, R. M.; McMillin, D. R. *Photochem. Photobiol.* **1989**, *50*, 711–716.
 (31) Kirchhoff, J. R.; Gamache, R. E., Jr.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380–2384.
 (32) Palmer, C. E. A.; McMillin, D. R. *Inorg. Chem.* **1987**, *26*, 3837–3840.

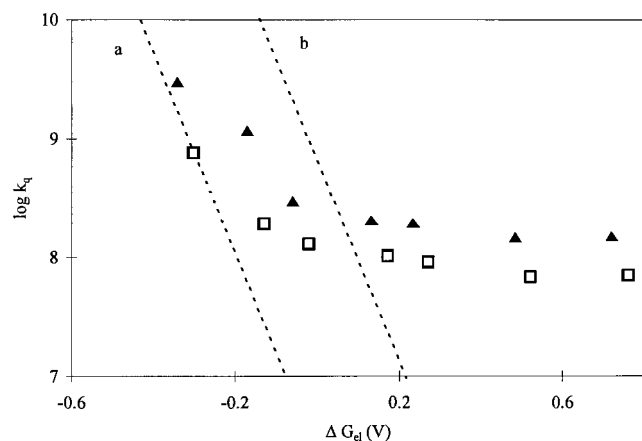


Figure 2. Quenching data for ferrocenes and $\text{Cu}(\text{dpp})_2^+$ (\square) and $\text{Cu}(\text{dipp})_2^+$ (\blacktriangle) in CH_2Cl_2 at room temperature. The driving force (ΔG_{el}) for electron-transfer quenching is most positive for $\text{Fe}(\text{CpAc})_2$ and most negative for FeCp^*_2 . Dashed line a (b) is a plot of eq 1 under the assumption that $k_{\text{qq}} = 4.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{**} = 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ($1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

in solution, time-resolved Raman measurements indicate that the excitation tends to localize within one of the heteroaromatic ligands,³³ and the $\text{Cu}^{2+}\text{--NN}^-$ charge distribution that results is the basis of the dipole moment.

The best indicator of the energy available in the photoexcited complex is ${}^3E_{00}$, the energy of the zero–zero transition of the ${}^3\text{CT}$ state. This is available from the zero–zero energy of the ${}^1\text{CT}$ state after allowance for the ${}^1\text{CT}/{}^3\text{CT}$ splitting which is about 1400 cm^{-1} .^{9,31} A reasonable estimate of ${}^1E_{00}$ is the energy where the emission intensity is 10% of the maximum on the high-energy side of the corrected ${}^1\text{CT}$ emission spectrum.³⁴ The choice of the 10% mark comes from the fact that this is the point at which the absorption and emission spectra of $\text{Cu}(\text{dpp})_2^+$ cross after normalization of the lowest energy absorption band and the (corrected) singlet emission to the same height.³⁵ The ${}^3E_{00}$ values obtained in this way appear in Table 3; previous values reported for the dpp and tptap complexes are 1.8 and 1.65 V, respectively.^{9–11}

Excited-State Quenching. Figure 2 shows that the quenching results with the dipp complex are qualitatively similar to previous observations involving $\text{Cu}(\text{dpp})_2^+$.¹¹ (Except for the data for the acetylated ferrocenes, the quenching results for the dpp system are from a prior investigation.¹¹) For any given quencher, the rate constant is greater for the dipp system than the dpp analogue. The ${}^3E_{00}$ value is higher for the dipp complex, at least in part because the sterically demanding isopropyl substituents inhibit structural relaxation within the excited state and enforce a more rigid pseudotetrahedral geometry upon the copper center.²² However, there is a nearly compensating drop in the reduction potential of the bound phenanthroline such that the excited-state potential ${}^*E_{0}^{+/0}$ is very similar for the two systems. There are some important differences in the quenching data involving the $\text{Cu}(\text{tptap})_2^+$ system, which shows the widest spread in k_{q} values. In comparison with the other two complexes, the tptap complex has the lowest ${}^3E_{00}$ value; nevertheless, the ${}^*E_{0}^{+/0}$ is relatively positive because the ligand reduction occurs at a much less cathodic, i.e., negative, potential. With this system Figure 3 shows that the k_{q} values reach a

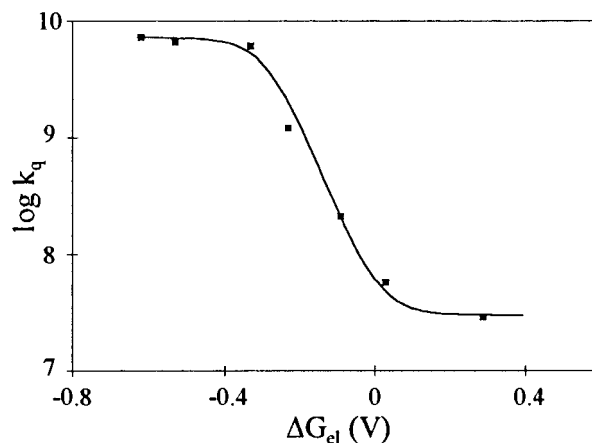


Figure 3. Quenching data for ferrocenes and $\text{Cu}(\text{tptap})_2^+$ in CH_2Cl_2 at room temperature. The most reducing ferrocene is $\text{Fe}(\text{CpMe}_4)_2$, and the least reducing is $\text{Fe}(\text{CpAc})_2$. The line is the fit to eq 2 with the assumption that $k_{\text{d}} = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{**} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{qq}} = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $k_{\text{en}} = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

diffusion plateau for the most reducing ferrocenes and that they fall off as the ferrocene potential increases.

Net Photochemistry. There is evidence for a net photoreaction between $\text{Cu}(\text{tptap})_2^+$ and certain ferrocenes. After an extended period of irradiation, samples containing decamethyl ferrocene show evidence of bleaching in the vicinity of 450 nm and the growth of an absorbance at ca. 780 nm. Control experiments show that these changes are consistent with the loss of the original copper(I) complex and formation of the ferrocenium ion, $\text{Fe}(\text{Cp}^*)_2^+$. In the dark the original solution shows no changes in absorbance over periods of days, and with the less-reducing diacetylferrocene, there is no evidence of a reaction in the presence or the absence of light. It is worth noting that no significant photoproduct formation occurs on the time scale of a typical quenching experiment. Hence, the presence of photoproducts does not complicate the analysis of the quenching data.

Discussion

Quenching Pathways. The plots in Figures 2 and 3 show that the quenching rate increases as the driving force (ΔG_{el}) for electron transfer from the ferrocene to the ${}^3\text{CT}$ state increases. These results provide clear-cut evidence for the importance of the electron-transfer quenching mechanism. Further evidence comes from the observation of net production of $\text{Fe}(\text{Cp})_2^+$ in conjunction with the tptap system. The net photochemistry is perhaps surprising because back electron transfer should be a spontaneous process; however, the $\text{Cu}(\text{NN})_2^0$ systems in general are prone to decomposition and formation of copper metal.²² Production of colloidal copper could explain why the reduction is at least partially irreversible. A referee pointed out that the ferrocenium ions may be unstable and that there is a report which suggests that this effect produces a net photoreaction with ruthenium(II) analogues.³⁶ The same reaction may occur in the present system as well; however, the decomposition of ferrocenium typically requires oxidizing conditions.³⁷ Moreover, the 580 nm band of $\text{Fe}(\text{Cp}^*)_2^+$ is plainly evident in the solution after photoreaction has occurred.

(33) McGarvey, J. J.; Bell, S. E. J.; Gordon, K. C. *Inorg. Chem.* **1988**, *27*, 4003–4006.

(34) Adamson, A. W. *J. Chem. Educ.* **1983**, *60*, 797–802.

(35) Grosshenny, V.; Harriman, A.; Romero, F. M.; Ziessel, R. *J. Phys. Chem.* **1996**, *100*, 17472–17484.

(36) Choua, S.; Kirsch-De Mesmaeker, A.; Jacquet, L.; Marzin, C.; Chabert, N. *J. Photochem. Photobiol. A: Chem.* **1996**, *99*, 127–136.

(37) Fehlhammer, W. P.; Moinet, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *158*, 187–191.

In all cases the reaction involves the ^3CT excited state. The ^1CT state has an important influence on the emission only because the radiative rate constant for the singlet state is several orders of magnitude greater than that of the triplet state.³¹ Meaningful participation of the singlet state requires such a kinetic differential because the Boltzmann factor reveals that the ratio of the populations of the singlet and triplet CT states is ca. 5×10^{-4} . Due to the difference in driving force, the rate enhancement for electron-transfer quenching of the ^1CT state is just a factor of 30. Therefore, it is safe to ignore the singlet state in the quenching analysis.

Energy-transfer quenching is also feasible because estimates of the $^3E_{00}$ of ferrocene range from 1.9 to 1.7 V^{38,39} to as low as 1.1 V.⁴⁰ In view of the fact that the d–d excitation bands occur at similar energies for FeCp_2 and FeCp_2^* ,²⁵ substituents probably have a minor influence on the $^3E_{00}$ value. Consequently, in light of the structural homology within the series,⁴¹ the rate of energy-transfer quenching is apt to be roughly constant throughout the series. That explains the near-plateaus in the quenching profiles in the $\Delta G_{\text{el}} > 0$ region of Figure 2. However, the log plots are not completely flat in this region, so the substituents evidently have some influence on the energetics. The drop in rate is particularly obvious in switching from alkyl to acyl substituents, and this could easily be due to differences in the $^3E_{00}$ values of the two types of ferrocene. The falloff in the plateau height as the $^3E_{00}$ of the donor drops provides additional supporting evidence for energy-transfer quenching in light of the theory developed by Balzani and co-workers.⁴¹ This theory clearly shows that the rate of energy-transfer quenching increases with the driving force of reaction.⁴¹

Quenching with $\text{Cu}(\text{dipp})_2^+$. Studies of the dipp complex provide a test of the influence the bulky isopropyl substituents have on excited-state reactivity. This effect is worth considering because a prior study concluded that the inner-sphere reorganizational energy of the copper center has an important impact on the kinetics of electron-transfer quenching.¹¹ The barrier arises because of the different structural preferences of the copper(II) and copper(I) oxidation states that formally exist in systems such as $^*\text{Cu}(\text{dpp})_2^+$ and $\text{Cu}(\text{dpp})_2^0$, respectively. The expectation is that bulky isopropyl substituents will impose a similar pseudotetrahedral coordination geometry on both forms. Consistent with a smaller degree of structural relaxation in the excited state, the dipp complex has a noticeably higher $^3E_{00}$ than the dpp analogue. However, due to the influence alkyl substituents have on the ground-state reduction potential, there is virtually no difference in the two excited-state reduction potentials (Table 3). The presence of the bulky isopropyl substituents does, however, enhance the quenching kinetics. In contrast to the results with the dpp complex, the quenching rate for octamethylferrocene reacting with the dipp complex significantly exceeds that of energy-transfer quenching. In fact, electron-transfer quenching is such a facile process with the dipp complex that the onset of diffusion control is becoming evident when decamethyl ferrocene is the quencher. In accordance with relative Marcus theory,^{6,42,43} eq 1 provides an estimate the self-exchange rate for a $^*\text{Cu}(\text{NN})_2^+/\text{Cu}(\text{NN})_2^0$ couple:

$$k_{\text{el}} = (k_{**}k_{\text{qq}}K_{\text{el}})^{1/2} \quad (1)$$

where k_{el} represents the rate constant for electron-transfer quenching, k_{**} and k_{qq} represent the rate constants for the self-exchange reactions of the excited state and the quencher, respectively, and K_{el} designates the equilibrium constant for the electron transfer. On the basis of quenching by decamethylferrocene, $k_{**} \approx 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the dpp complex; similarly, the quenching rate for octamethyl ferrocene predicts that $k_{**} \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the dipp system. Both calculations assume that $k_{\text{qq}} = 4.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, the reported rate constant for the self-exchange reaction of decamethylferrocene in CH_2Cl_2 .⁴⁴ Curve b in Figure 2 is the calculated line that the quenching data follows if electron-transfer quenching is the sole path available, if the self-exchange rate of the excited state is diffusion controlled ($k_{**} = 10^{10} \text{ M}^{-1} \text{ s}^{-1}$), and if each ferrocene has the same self-exchange rate as decamethyl ferrocene. Curve a in the same figure is the corresponding line that applies when $k_{**} = 2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ as obtained for the dpp complex. Thus the offset between curves a and b reveals that the inner-sphere reorganizational barrier acts as a kind of overpotential that retards the rate of electron transfer to the dpp complex. The shift associated with reductive quenching of the dipp complex is obviously smaller. This is a consequence of the geometric constraints presented by the sterically demanding isopropyl groups.

Quenching with $\text{Cu}(\text{tptap})_2^+$. With the higher $^*E_{0+0}$ value, reductive quenching is the dominant quenching pathway for the tptap complex in every case except diacetyl ferrocene. Electron-transfer quenching is a slightly endoergonic process for $\text{FeCp}(\text{CpAc})$, but this still turns out to be the important pathway. On the other hand, the observed rate of quenching by $\text{Fe}(\text{CpAc})_2$ exceeds the value extrapolated for electron-transfer quenching by about an order of magnitude. As a consequence, the quenching rate for diacetyl ferrocene alone determines the “background” rate of energy-transfer quenching.

Electron-transfer quenching is so efficient with the tptap complex that diffusion control sets in for the systems that have a high driving force (Figure 3). Accordingly, the appropriate theoretical model is

$$1/k_{\text{q}} = 1/k_{\text{d}} + 1/(k_{\text{el}} + k_{\text{en}}) \quad (2)$$

where k_{d} denotes the diffusion rate, and k_{en} denotes the rate constant for energy-transfer quenching.⁶ Substitution of eq 1 into eq 2 gives $k_{**} = 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ from the fit of the data given in Figure 3. The estimate $k_{\text{en}} = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ comes from the data point for diacetylferrocene, and the average of the quenching rates obtained for the octa- and pentamethylferrocene derivatives provides the value $k_{\text{d}} = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The other assumption is that $k_{\text{qq}} = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for all the ferrocenes; this is the average of the self-exchange rates reported for ferrocene and decamethylferrocene.⁴⁴ The k_{**} value obtained for the $^*\text{Cu}(\text{tptap})_2^+/\text{Cu}(\text{tptap})_2^0$ couple is closer to that of the dipp complex than that of the seemingly more analogous dpp system. This is undoubtedly due to the presence of the extra phenyl substituents in the 2,7 positions of the tptap ligand. They act to restrict the rotational freedom of the phenyl groups that are adjacent to the chelating nitrogen centers. This in turn constrains geometrical relaxation within the excited state and renders the complex more rigid. The same steric forces are clearly at work in the ground state as the absorption spectrum

(38) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161–4167.

(39) Chapple, A. P.; Vikesland, J. P.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *50*, 81–84.

(40) Balzani, V.; Bolletta, F.; Moggi, L. *Spectrosc. Lett.* **1978**, *11*, 525–535.

(41) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2153.

(42) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111–1122.

(43) Prasad, D. R.; Ferraudi, G. *J. Phys. Chem.* **1982**, *86*, 4037–4040.

(44) Nielson, R. M.; McManis, G. E.; Golovin, M. N.; Weaver, M. J. *J. Phys. Chem.* **1988**, *92*, 3441–3450.

Table 4. Excited-State Oxidants

excited state/ product	*E ₀ , V vs SHE	k _{**} , M ⁻¹ s ⁻¹	active orbital	ref
*Eu _(aq) ^{3+/2+}	+1.65	10 ⁻¹²	4f	a
*Ru(bpy) ₃ ^{2+/+}	+0.8	10 ⁸	dπ	b
Cu(dpp) ₂ ⁺⁰	+0.1 ^c	10 ⁵	dσ	d
Cu(tptap) ₂ ⁺⁰	+0.6 ^c	10 ⁷	dσ	d

^a Reference 47. ^b Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717–2738. ^c Referenced to E₀(Fc⁺⁰) = +0.4 vs SHE; Heusler, K. E.; Lorentz, W. J. In *Standard Potentials in Aqueous Solution*; Bard, A. J., Parsons, R., Jordan, J., Eds.; Marcel Dekker: New York, 1985; pp 391–412. ^d This work.

of the tptap complex is consistent with approximate D_{2d} geometry. In contrast, due to a ground-state distortion,^{27,28} the absorption spectrum of the dpp complex exhibits a very pronounced shoulder on the long-wavelength side of the CT absorption spectrum.

In the final analysis the tptap complex represents something of a compromise. True, it offers a CT excited state that is a considerably better oxidant than any copper phenanthroline studied to date. However, the lifetime is relatively short. In large part this may be a simple consequence of the energy-gap law because the ³E₀₀ energy is fairly low. At the same time the electron distribution within the “radical-anion” ligand of the excited state undoubtedly differs from that of a phenanthroline complex. This may result in structural changes that intrinsically influence the radiationless decay process.

Conclusions

As anticipated by Kirsch-De Mesmaeker and co-workers,¹⁰ the reducibility of the tptap ligand enhances the excited-state reactivity of the Cu(tptap)₂⁺ system toward quenchers capable of giving up an electron. However, the ferrocenes used here are more effective quenchers than hydroquinone, for which the potential depends on complicating pH-dependent equilibria.⁴⁵ Net oxidation of reducing ferrocenes occurs in methylene chloride with a low quantum yield probably because of the instability of the reduction product Cu(tptap)₂⁰. The potentials and self-exchange rates in Table 4 reveal that reductive quenching of the tptap complex should be almost as common as it is for the *Ru(bpy)₃²⁺ ion. This is an intriguing result because the reduction of copper-containing systems such as *Cu(dpp)₂⁺ involves the population of a metal–ligand antibonding

(45) Plancherel, D.; Vos, J. G.; von Zelewsky, A. *J. Photochem.* **1987**, *36*, 267–278.

(dσ*) orbital, and the structural reorganization that ensues poses a barrier to electron-transfer quenching.^{9,11} G. J. Meyer and co-workers exploited a related effect when they studied covalently linked copper(I) donor–acceptor compounds.⁴⁶ In their systems the barrier associated with the copper(II)/copper(I) couple inhibits back electron transfer and prolongs the lifetime of the charge-separated state. Within the context of Marcus theory, the influence of the reorganizational energy shows up most clearly in the magnitude of the rate constant for the self-exchange reaction. As Table 4 shows the k_{**} value is much larger for the tptap complex than for the dpp complex. This appears to be a consequence of the steric constraints that the 2,7-phenyl groups impose on the orientation of the other phenyl substituents that are next to the chelating nitrogens. This effect is the subject of ongoing work. The bulky isopropyl substituents in the Cu(dipp)₂⁺ system also provide for a favorable k_{**} value, but the excited-state potential is rather low in this case. For the sake of comparison Table 4 also includes the data for the *Eu(aq)³⁺ system which is notoriously slow to undergo electron-transfer quenching. Here, the problem is a weak transmission coefficient due to the need to populate a well-buried 4f orbital.⁴⁷

Finally, the quenching data reveal that the rate of energy-transfer to ferrocene is very sensitive to the ³E₀₀ value of the copper complex. In line with this trend energy-transfer occurs at a diffusion-controlled rate when *Ru(bpy)₃²⁺ is the donor and the driving force is higher (³E₀₀ = 2.15 V⁴⁸). However, a Franck–Condon barrier may also suppress the rate of energy-transfer quenching for the copper systems. As Balzani and co-workers have pointed out, such a barrier arises whenever formation of the excited state involves significant structural reorganization.³⁹

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Supporting Information Available: Plots of the absorption and emission spectra of Cu(dipp)₂⁺ and Cu(tptap)₂⁺ in CH₂Cl₂ (2 pages). Ordering information is given on any current masthead page.

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(46) Ruthkosky, M.; Kelly, C. A.; Zaros, M. C.; Meyer, G. J. *J. Am. Chem. Soc.* **1997**, *119*, 12004–12005.

(47) Christensen, K. M.; Bakac, A.; Espenson, J. H. *Chem. Phys.* **1993**, *176*, 359–365.

(48) Lee, E. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8562–8564.