

in the case of  $\text{Ru}(\text{dpt})_2^{2+}$  where steric effects are expected to hinder the  $k_{32}$  and  $k_{3d}$  steps. Since  $\text{SCN}^-$  falls high in the spectrochemical series and since the CT bands of the photoproduct are red-shifted, the gap between the  $^3\text{d-d}$  state and the  $^3\text{CT}$  state of the photoproduct is likely to be enhanced over that of  $\text{Ru}(\text{dpt})_2^{2+}$ . In line with this reasoning, the isothiocyanate complex is hardly photo-reactive; it exhibits an emission at 77 K which maximizes at 767 nm (uncorrected) and has a lifetime of ca. 2  $\mu\text{s}$ .

The case of  $\text{Ru}(\text{tsite})_2^{2+}$  is interesting because it is a reasonably good emitter in fluid solution at room temperature (Table I). The 4,4' and 4'' phenyl substituents are unlikely to affect significantly the energy of the  $^3\text{d-d}$  state, but they undergo mesomeric interactions with the terpy moiety and therefore could influence the energy of the  $^3\text{CT}$  state. Indeed, from the absorption data in Table I, it appears that the CT maximum occurs at lower energy in the tsite complex. Moreover, the mesomeric effect may be enhanced in the thermally equilibrated excited state where the ligand assumes radical anion character. Stabilization of the  $^3\text{CT}$  state relative to the  $^3\text{d-d}$  state would increase the barrier to the  $k_{12}$  step and enhance the lifetime of the CT excited state.

Although Scheme I has been applied only qualitatively, it seems capable of explaining all the available results pertaining to  $\text{Ru}(\text{trpy})_2^{2+}$  derivatives. As an alternative, one might invoke a model

which assumes a single excited state of mixed CT and d-d character. Variations in the series would then be attributed to differences in the proportion of d-d character and/or the activation energy associated with the dissociative step. The multiple state model is preferred because of the diverse observations which show that these states often coexist and mutually determine the photochemical and photophysical properties of related d<sup>6</sup> complexes.<sup>35-39</sup>

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**Registry No.**  $\text{Ru}(\text{dpt})_2^{2+}$ , 94619-67-7;  $\text{Ru}(\text{dpt})(\eta^2\text{-dpt})(\text{NCS})^+$ , 94619-68-8;  $\text{SCN}^-$ , 302-04-5.

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## Quenching Studies of $^*\text{Cu}(\text{dpp})_2^+$ . Evidence for Competitive Electron-Transfer and Energy-Transfer Quenching by $\text{Cr}(\text{acac})_3$ Derivatives

Roland E. Gamache, Jr., Rosemary A. Rader, and David R. McMillin\*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. Received August 13, 1984

**Abstract:** The kinetics of quenching  $^*\text{Cu}(\text{dpp})_2^+$ , the  $^3\text{d}-\pi^*$  excited state of  $\text{Cu}(\text{dpp})_2^+$  (dpp = 2,9-diphenyl-1,10-phenanthroline), by a series of  $\text{Cr}(\text{acac})_3$  derivatives and a series of nitroaromatics have been studied in  $\text{CH}_2\text{Cl}_2$  solution at 20 °C. For the nitroaromatic compounds, the quenching rate falls off as the electrode potential of the quencher ranges below that of  $^*\text{Cu}(\text{dpp})_2^+$ , consistent with an electron-transfer mechanism. The results were analyzed by a variation of the Marcus theory, and the self-exchange rate for the  $\text{Cu}(\text{dpp})_2^{2+}/^*\text{Cu}(\text{dpp})_2^+$  system was estimated to be  $8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The  $\text{Cr}(\text{III})$  quenchers span a much wider range of electrode potentials and are also capable of undergoing energy-transfer quenching via the low-lying doublet excited states. As a result the quenching rate constant exhibits a more complex dependence on the free energy of electron-transfer quenching. In the exergonic region, the rate plateaus at the diffusion limit; as electron-transfer quenching becomes endergonic, the rate initially decreases and then levels off again at ca.  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This behavior is explained as a changeover from electron-transfer to energy-transfer quenching where the latter process occurs at a roughly constant rate throughout the series. When electron-transfer quenching is prominent, the average self-exchange rate for the  $\text{Cr}(\text{III})/\text{Cr}(\text{II})$  couples is estimated to be  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , suggesting that the  $\text{Cr}(\text{II})$  forms are low spin. The utility of  $^*\text{Cu}(\text{dpp})_2^+$  as a redox reagent and novel aspects of the homologous series of  $\text{Cr}(\text{acac})_3$  derivatives as quenchers are discussed.

There is continuing interest in the photochemical and photophysical properties of charge-transfer (CT) excited states of transition-metal complexes, partly because such states have been found to be useful in various schemes for energy conversion and fuel formation.<sup>1,2</sup> The long-lived charge-transfer excited state(s) of  $\text{Ru}(\text{bpy})_3^{2+}$ , where bpy denotes 2,2'-bipyridine, has been studied in great detail, especially by the use of quenching methods.<sup>2-6</sup> It

is prone to electron-transfer quenching, and the redox properties of the state are well established.<sup>7-9</sup> Defining the scope and the limitations of such excited-state reagents depends upon the characterization of many more systems. One of the aims of the present work has been to characterize the redox properties of the d<sup>10</sup> complex  $\text{Cu}(\text{dpp})_2^+$  (dpp denotes 2,9-diphenyl-1,10-phenanthroline), an ion recently found to exhibit a long-lived CT excited state in  $\text{CH}_2\text{Cl}_2$  solution.<sup>10</sup> Here we report that various

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**Table I.** Data for Cr(III) Quenchers

complex	neutral ligand	synthetic method
Cr(hfac) <sub>3</sub>	1,1,1,5,5,5-hexafluoro-2,4-pentanedione <sup>a</sup>	<i>b</i>
Cr(tfzac) <sub>3</sub>	4,4,4-trifluoro-1-phenyl-1,3-butanedione <sup>a</sup>	<i>c</i>
Cr(tta) <sub>3</sub>	thenoyltrifluoroacetone <sup>e</sup>	<i>c</i>
Cr(tfac) <sub>3</sub>	1,1,1-trifluoro-2,4-pentanedione <sup>a</sup>	<i>c</i>
Cr(dbm) <sub>3</sub>	1,3-diphenyl-1,3-propanedione <sup>e</sup>	<i>c</i>
Cr(pdo) <sub>3</sub>	1,3-propanedial	<i>d</i>
Cr(bzac) <sub>3</sub>	1-phenyl-1,3-butanedione	<i>a</i>
Cr(acac) <sub>3</sub>	2,4-pentanedione <sup>e</sup>	<i>f</i>

<sup>a</sup>Purchased from Eastman. <sup>b</sup>Sievers, R. E.; Moshier, R. W.; Morris, M. L. *Inorg. Chem.* **1962**, *1*, 966-967. <sup>c</sup>Charles, R. G. *Inorg. Synth.* **1966**, *8*, 138-140. <sup>d</sup>Collman, J. P.; Kittleman, E. T.; Hunt, W. S.; Moore, N. A. *Inorg. Synth.* **1966**, *8*, 141-143. <sup>e</sup>Purchased from Aldrich. <sup>f</sup>Fernelius, W. C.; Blanch, J. E. *Inorg. Synth.* **1957**, *5*, 130-131.

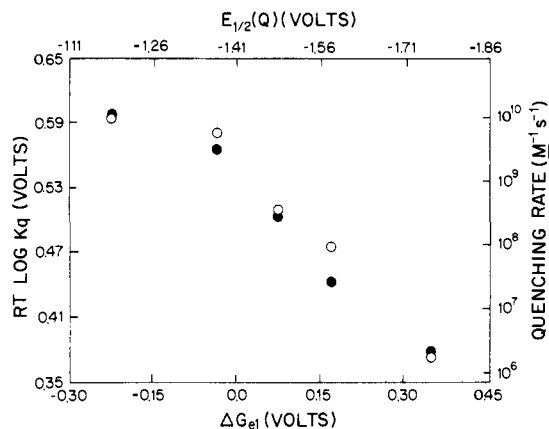
nitroaromatic compounds quench the CT excited state of Cu(dpp)<sub>2</sub><sup>+</sup>, denoted \*Cu(dpp)<sub>2</sub><sup>+</sup>, by an electron-transfer mechanism. An analysis of these results provides an estimate of the rate constant for the self-exchange reaction of \*Cu(dpp)<sub>2</sub><sup>+</sup>. A second aim has been to explore the utility of a potentially valuable series of quenchers based on 1,3-propanedionate derivatives of Cr(III). This series is remarkable because it spans a wide range of potentials; at the same time, the low-lying d-d states of these compounds are virtually isoenergetic.<sup>11</sup> For the Cr(III) quenchers with the more positive electrode potentials, the quenching rate exhibits classic behavior for electron-transfer quenching—the rate increases with the driving force and finally saturates at the diffusion limit. From these data we obtain an estimate of the average rate constant for the self-exchange reactions of the Cr(III)/Cr(II) couples involved. On the other hand, when the electron-transfer process becomes endergonic, the quenching rate constant plateaus again, at a value around 10<sup>7</sup> M<sup>-1</sup> s<sup>-1</sup>. This is attributed to a parallel energy-transfer pathway to quenching which takes over when the E<sub>1/2</sub> of the chromium species is unfavorable for electron transfer.

### Experimental Section

**Materials and Methods.** Cu(dpp)<sub>2</sub>BF<sub>4</sub> was prepared as before.<sup>10</sup> The Cr(III) quenchers were prepared according to the procedures cited in Table I with minor modifications. For example, Cr(pdo)<sub>3</sub> was prepared by using 1,1,3,3-tetramethoxypropane instead of 1,1,3-trimethoxy-3-ethoxypropane. Cr(hfac)(tfzac)<sub>2</sub> was prepared by a variation of the method developed for Cr(hfac)<sub>3</sub> and was purified by elution from a silica gel column. The composition of the mixed-ligand complex was established from the mass spectrum which was obtained by using chemical ionization. The complex eluted as a single band and presumably consisted of only one geometric isomer. *cis*- and *trans*-Cr(bzac)<sub>3</sub> were resolved by eluting from a silica gel column. No evidence for geometric isomers was found in the other cases where unsymmetrical ligands were involved. Presumably, the *cis* isomers were present in negligible quantities.<sup>12</sup> The Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and CrCl<sub>3</sub> starting materials were obtained from Fisher Scientific; CrCl<sub>3</sub>·6H<sub>2</sub>O was obtained from Baker Chemical. The 4,4'-dinitrophenyl was obtained from Eastman, and the nitrobenzene was from Fisher Scientific. All other nitroaromatics were from Matheson, Coleman and Bell. Purification was achieved by distillation or recrystallization from acetone. Spectral-grade methylene chloride was used for the lifetime measurements and was obtained from Baker Chemical. For the electrochemical measurements, the CH<sub>2</sub>Cl<sub>2</sub> was swirled over alumina and filtered. [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub> was prepared from [(*n*-Bu)<sub>4</sub>N]I and was recrystallized several times before use.

In the lifetime studies, all samples were deoxygenated by repetitive freeze/pump/thaw cycles. The Cu(dpp)<sub>2</sub><sup>+</sup> was excited at 440 nm or at a minimum in the absorbance spectrum of the quencher, and lifetimes were calculated from the slopes of standard log plots. For the electrochemical measurements, samples were dissolved in methylene chloride that was 0.1 M in [(*n*-Bu)<sub>4</sub>N]PF<sub>6</sub>. The samples were degassed by purging with a solvent-saturated stream of nitrogen for 20 min. Half-wave potentials were obtained from the cyclic voltammograms by averaging the anodic and cathodic current maxima. The scan rate was 0.1 V s<sup>-1</sup>.

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**Figure 1.** Correlation between the rate of quenching \*Cu(dpp)<sub>2</sub><sup>+</sup> by nitroaromatics and the free energy of electron transfer. The data are from a CH<sub>2</sub>Cl<sub>2</sub> solution at 20 °C. The solid circles represent experimental points, the open circles calculated points. *k<sub>q</sub>* for 4,4-dinitrophenyl was calculated assuming a *k<sub>QQ</sub>* value which was the average of the values reported for the other nitroaromatics (Table II). This point was omitted in the calculation of *k<sub>q</sub>*.

**Apparatus.** An EG&G Princeton Applied Research Model 2100 nitrogen-pumped dye laser was used as the pulsed light source. The instrumental pulse width was ca. 5 ns at half peak height. An RCA 4840 or an RCA 931 photomultiplier tube, powered by a Pacific Instruments Model 227 high-voltage power supply and hard-wired for fast response,<sup>13</sup> was used to monitor the luminescence. The signal was sampled with an EG&G Model 162 boxcar averager which included a Model 165 gated integrator and which was interfaced to an Apple II Plus computer via a Cyborg Model 91A interface. The data were stored and processed with user-written software. Fluorescence spectra were obtained with a Perkin-Elmer MPF-44B spectrometer; absorbance spectra were run on a Cary 17D spectrophotometer. A Bioanalytical Systems Model CV-1A cyclic voltammetry unit was used in the electrochemical studies with a Pt-bead working electrode, a AgCl/Ag reference electrode, a Pt wire auxiliary electrode, and a Hewlett-Packard 7015B X-Y recorder.

### Results

The E<sub>1/2</sub> values, measured in CH<sub>2</sub>Cl<sub>2</sub> and referenced against the Fe(Cp)<sub>2</sub><sup>+</sup>/Fe(Cp)<sub>2</sub> couple in the same solvent, are reported in Table II. The ferrocene couple is reported to have a potential of 0.286 V vs. SCE in acetone<sup>14</sup> which has a dielectric constant and a polarizability similar to that of CH<sub>2</sub>Cl<sub>2</sub>. Hence, as a rough guide, one can add 0.29 to the potentials reported in order to convert to an SCE reference electrode. The potential differences within the chromium series are on the whole similar to those previously observed in dimethyl sulfoxide.<sup>11</sup> We were unable to measure the potential for Cr(acac)<sub>3</sub>; the value reported is an extrapolation from the data in ref 11. The separation between the anodic and cathodic peaks in the cyclic voltammograms ranged between 120 and 200 mV for the chromium complexes and was much larger (200-500 mV) for the nitroaromatics.

In the initial stages of the work, we attempted to measure quenching constant (*k<sub>q</sub>*'s) by monitoring the luminescence intensity as a function of quencher concentration. Nonlinear Stern-Volmer plots were observed due to inner-filter effects from the Cr(III) systems, all of which absorb in the visible. The corrections proposed by Demas and Adamson<sup>15</sup> did not eliminate the problem. Consequently, we resorted to the lifetime method, obtaining *k<sub>q</sub>*'s from graphs of the data according to eq 1, where  $\tau$  is the emission lifetime when the quencher concentration is [Q] and  $\tau_0$  is the emission lifetime in the absence of quencher.<sup>6</sup> The *k<sub>q</sub>* values and

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[Q] \quad (1)$$

other relevant data are compiled in Table II; plots of log *k<sub>q</sub>* vs. ΔG<sub>et</sub>, the free energy of electron-transfer quenching, are presented

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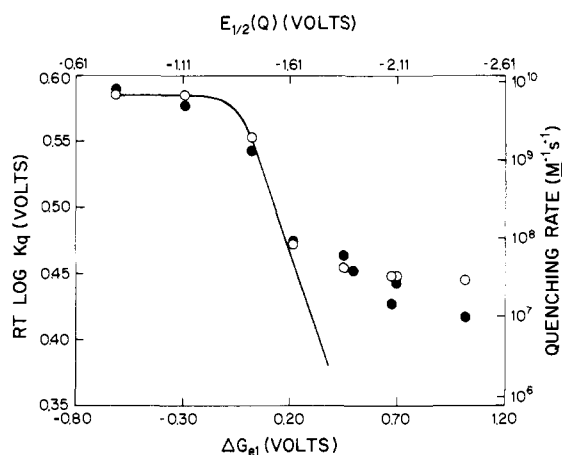
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Table II. Quenching Analysis

quencher	$k_q, M^{-1} s^{-1}$	$E_{1/2}, V^a$	$k_{QQ}, M^{-1} s^{-1} b$	10Dq, V <sup>c</sup>	$\Delta E(^2E \leftarrow ^4A_{2g}), V^d$	$\beta^d$
<i>p</i> -dinitrobenzene	$1.1 \times 10^{10}$	-1.18	$6.5 \times 10^9$			
<i>m</i> -dinitrobenzene	$3.2 \times 10^9$	-1.37	$5.6 \times 10^9$			
4,4'-dinitrobiphenyl	$2.9 \times 10^8$	-1.48				
1-chloro-4-nitrobenzene	$2.9 \times 10^7$	-1.58	$8.6 \times 10^8$			
nitrobenzene	$2.4 \times 10^6$	-1.76	$3.3 \times 10^8$			
Cr(hfac) <sub>3</sub>	$7.7 \times 10^9$	-0.79		2.16	1.56	0.68
Cr(hfac)(tfbzac) <sub>2</sub>	$4.7 \times 10^9$	-1.12				0.67 <sup>e</sup>
Cr(tfbzac) <sub>3</sub>	$1.3 \times 10^9$	-1.43		2.17	1.52	0.66
Cr(tta) <sub>3</sub>	$2.0 \times 10^9$	-1.43				0.67 <sup>e</sup>
Cr(tfac) <sub>3</sub>	$9.5 \times 10^7$	-1.64		2.19	1.51	0.66
Cr(dbm) <sub>3</sub>	$6.5 \times 10^7$	-1.87		2.17	1.50	0.65
Cr(pdo) <sub>3</sub>	$3.9 \times 10^7$	-1.91		2.23	1.54	0.66
<i>c</i> -Cr(bzac) <sub>3</sub>	$1.6 \times 10^7$	-2.09		2.20	1.56	0.68
<i>t</i> -Cr(bzac) <sub>3</sub>	$2.8 \times 10^7$	-2.11		2.20	1.56	0.68
Cr(acac) <sub>3</sub>	$1.0 \times 10^7$	-2.43		2.21	1.61	0.70

<sup>a</sup>The potentials listed are for CH<sub>2</sub>Cl<sub>2</sub> solutions and are referenced to the ferrocene couple as discussed in the text. <sup>b</sup>The rate constants for the self-exchange reactions have been corrected on the assumption that the outer-sphere contribution to the activation energy is given as  $\Delta G_o^* = (n^2/4r)((1/n_D) - (1/D))$  where  $n$  is the number of electrons transferred,  $r$  is the sum of the radii of the two species,  $n_D$  is the refractive index and  $D$  is the static dielectric constant.<sup>26</sup> For CH<sub>2</sub>Cl<sub>2</sub>  $n_D = 1.47242$  and  $D = 9.00$ , and for CH<sub>3</sub>CN  $n_D = 1.34423$ ,  $D = 37.5$ ;  $n = 1$ , and  $r$  is approximately equal to 8.4 Å. <sup>c</sup>Reference 11. <sup>d</sup>Reference 12, except as noted. <sup>e</sup>Average value for the series.



**Figure 2.** Correlation between the rate of quenching  $^*Cu(dpp)_2^+$  by the Cr(acac)<sub>3</sub> derivatives and the free energy of electron transfer. The data are from a CH<sub>2</sub>Cl<sub>2</sub> solution at 20 °C. The solid circles represent the experimental data, the open circles the calculated. The solid line is the predicted correlation if only electron-transfer quenching occurs and  $k_{QQ} = 1.9 \times 10^9 M^{-1} s^{-1}$ .

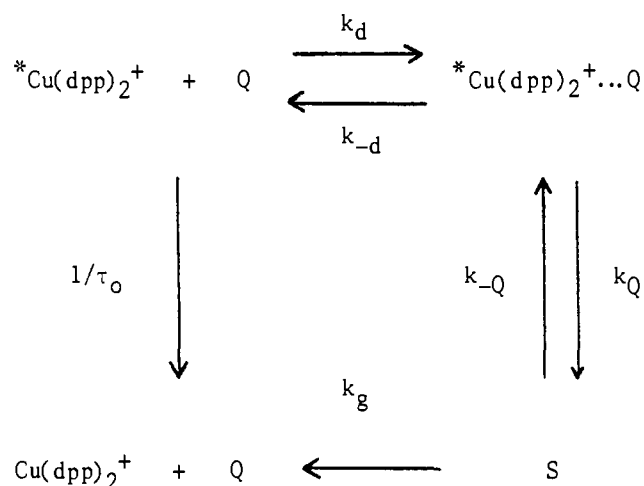
in Figures 1 and 2. In calculating  $\Delta G_{el}$ , the potential for the  $Cu(dpp)_2^{2+}/^*Cu(dpp)_2^+$  couple was taken as -1.41 V vs. ferrocene.<sup>16</sup>

As can be seen from Figure 1, the  $k_q$  values of the nitroaromatics are diffusion-limited when  $\Delta G_{el}$  is significantly exergonic, and the rate falls off monotonically as  $\Delta G_{el}$  becomes more and more positive. In contrast the Cr(III) quenchers exhibit a sigmoidal or "stepped" dependence on  $\Delta G_{el}$  (Figure 2). In this case  $k_q$  decreases from the diffusion-limited plateau as  $\Delta G_{el}$  increases toward 0, and it levels off again around  $10^7 M^{-1} s^{-1}$  in the endergonic region.

### Discussion

The photoluminescence from copper(I) complexes like  $Cu(dpp)_2^+$  is known to occur from redox-active metal-to-ligand charge-transfer excited states.<sup>17-20</sup> Actually, the emission is

### Scheme I



composite and involves (at least) two dynamically interconverting excited states separated by 1500–2000 cm<sup>-1</sup>.<sup>19</sup> In view of the energy gap and the radiative rate constants which have been resolved, the upper and lower levels have been assigned singlet and triplet parentage, respectively.<sup>19</sup> The fact that multiple excited states are involved may also be reflected in the measured  $k_q$  values. Thus, if the levels interconvert rapidly and are thermally equilibrated,  $k_q$  corresponds to a weighted average of the quenching constants of the individual levels.<sup>21</sup> This would complicate the interpretation of  $k_q$  values because  $\Delta G_{el}$  would be different for the two excited states; moreover, energy transfer from the charge-transfer singlet state to the doublet state of the Cr(III) complexes would be spin-forbidden. However, since the singlet and the triplet states of  $Cu(dpp)_2^+$  are well separated, the equilibrium population of the upper state is quite small, and  $k_q$  can be identified with the triplet excited state. The same is true if, as opposed to complete equilibration, only a steady-state condition is maintained.<sup>3</sup> Consequently, in the following we analyze the quenching reactions with a model which tacitly assumes that only one excited state is involved.

**Kinetic Scheme.** The minimal reaction sequence which can be used to describe the quenching is presented in Scheme I. In this scheme  $^*Cu(dpp)_2^+ \cdots Q$  denotes an encounter complex,  $k_Q$  designates an electron-transfer and/or an energy-transfer process, and S is a successor complex which is assumed to convert rapidly and irreversibly into the separated reagents in their ground

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electronic states. In principle, if electron-transfer quenching is involved, an additional process could be relevant, namely the separation and subsequent recombination of  $\text{Cu}(\text{dpp})_2^{2+}$  and  $\text{Q}^-$ . However, in view of the self-exchange rates of the species involved, vide infra, and the dielectric constant of  $\text{CH}_2\text{Cl}_2$ , the dissociation of the ion pair is unlikely to be important.

Analytical expressions for time-dependent concentrations of the species in Scheme I would involve unwieldy sums of exponentials.<sup>22</sup> A more useful equation is obtained if we make some simplifying and realistic approximations. We first treat the encounter complex as a steady-state species. This is justified since, in view of the level of quencher involved, the concentration of the encounter complex must be minute at all times compared with that of  $^*\text{Cu}(\text{dpp})_2^{2+}$ .<sup>23</sup> If we further assume that  $k_g \gg k_{-Q}$ , we arrive at eq 2, which when compared with eq 1 yields the ex-

$$\frac{d[{}^*\text{Cu}(\text{dpp})_2^{2+}]}{dt} = - \left[ \frac{1}{\tau_0} + \frac{k_d[\text{Q}]}{1 + \frac{k_{-d}}{k_Q}} \right] [{}^*\text{Cu}(\text{dpp})_2^{2+}] \quad (2)$$

pression for  $k_q$  presented in eq 3. The fact that the experimental

$$k_q = \frac{k_d}{1 + (k_{-d}/k_Q)} \quad (3)$$

decay curves gave rise to linear log plots is in accord with this model. The assumption that  $k_g \gg k_{-Q}$  is readily justified in the event of energy-transfer quenching by the Cr(III) complexes, as the  $k_{-Q}$  step is endergonic in all cases. On the other hand, as pointed out by Balzani and co-workers,<sup>24</sup> when electron-transfer quenching is involved and the  $k_Q$  step is endergonic, the  $k_g$  process could fall in the Marcus "inverted" region, where electron transfer is predicted to occur at a reduced rate.<sup>25,26</sup> The falloff, predicted for the electron-transfer rates when large driving forces are involved, has recently been observed in some unimolecular reactions.<sup>27</sup> However, several studies have shown that no significant depression in rate can be expected to occur for the recombination reactions discussed here.<sup>24,28-32</sup>

**Nitroaromatic Quenching.** Energy transfer from  $^*\text{Cu}(\text{dpp})_2^{2+}$  to the nitroaromatics is an unfavorable process due to the high triplet energies, e.g., 2.6 V for nitrobenzene.<sup>33</sup> Moreover, the pronounced falloff in the  $k_q$  value as  $\Delta G_{el}$  becomes positive (Figure 1) is the hallmark of electron-transfer quenching. As only modest structural changes are expected to attend these reactions, an outer-sphere pathway is likely. With this assumption we can relate the quenching rates to  $k_{QQ}$  and  $k_{**}$ , the rate constants for the self-exchange reactions of the  $\text{Q}/\text{Q}^-$  and the  $\text{Cu}(\text{dpp})_2^{2+}/^*\text{Cu}(\text{dpp})_2^{2+}$  couples, respectively, and  $K_{el}$  the equilibrium constant for the electron-transfer reaction. (The latter can be calculated from the  $E_{1/2}$  values in Table II.) In broad outline, our method parallels that of Prasad and Ferraudi.<sup>34</sup> The first step is to rewrite

eq 3 as in eq 4. The other relation needed is given in eq 5 where

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{(k_d/k_{-d})k_Q} \quad (4)$$

$k_{el}$  is the rate constant for the reduction of quencher Q by  $^*\text{Cu}(\text{dpp})_2^{2+}$ . This so-called "cross relation" is analogous to an equation

$$k_{el} = (k_{**}k_{QQ}K_{el})^{1/2} \quad (5)$$

first derived by Marcus.<sup>35-37</sup> More recently, Ratner and Levine have shown that eq 5 follows from a few general assumptions which are expected to be widely applicable.<sup>38,39</sup> If the  $k_g$  step in Scheme I is not rate-limiting and the quenching is by electron transfer, eq 4 and 5 can be combined to give eq 6. A least-squares

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{el}} \quad (6)$$

analysis of the data from the four systems with known  $k_{QQ}$  values,<sup>40</sup> corrected for solvent effects (Table II), reveals that the least-squares fit of the  $k_q^{-1}$  values obtains with  $k_{**} = 8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_d = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . These values are rough because of the assumptions behind eq 5,<sup>38,39</sup> but they appear to be reasonable estimates. The  $k_{**}$  value should be representative of a self-exchange reaction involving the  $\pi^*$  orbital of a coordinated phenanthroline or bipyridine ligand. Values of  $10^8$ – $10^9$  have previously been reported for such systems in aqueous media.<sup>41,42</sup> The  $k_d$  value we obtain is also plausible; a simple diffusion model predicts  $k_d = 8RT/3\eta = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  where  $\eta$  denotes the solvent viscosity.<sup>43</sup>

**Cr(III) Quenching.** In the exergonic region the quenching constants for the Cr(III) systems also vary inversely with  $\Delta G_{el}$ , consistent with electron-transfer quenching (Figure 2). However, the leveling off of the quenching constant when  $\Delta G_{el}$  becomes positive cannot be explained by an electron-transfer quenching mechanism; it predicts the behavior described by the solid line in Figure 2. The plateau in the endergonic region of the plot is doubtless an indication of a competing pathway to quenching. A similar stepped dependence on the driving force of the reaction has been observed in studies of the oxidation of  $\text{Eu}^{2+}(\text{aq})$  by a series of reactants, including several excited-state species.<sup>44</sup> These results were interpreted in terms of a switch from an outer-sphere to an inner-sphere reaction mechanism.<sup>1,44</sup> In studies of the quenching of a series of triplet aromatics by  $\text{Cr}(\text{dpm})_3$ , where dpm denotes 2,2,6,6-tetramethyl-3,5-heptanedionate, Wilkinson and Tsiamis have also reported a stepped dependence of the energy-transfer rate on the driving force for the reaction.<sup>45</sup> In this case the step, which occurs in the exergonic region of the plot, has been attributed to the onset of facile energy transfer to higher energy excited states of the acceptor.<sup>45,46</sup> We ascribe the lower plateau in Figure 2 to an energy-transfer pathway which occurs in parallel to the electron-transfer path. In accord with this hypothesis, Wilkinson and Tsiamis have previously reported that the energy-transfer and electron-transfer mechanisms are competitive in the quenching of triplet aromatics by  $\text{Cr}(\text{acac})_3$  systems.<sup>47</sup> As the luminescence quantum yields of the Cr(III) systems are quite

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(28) Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, 101, 6140–6142.

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(31) It is true, however, that as  $\Delta G_{el}$  becomes more positive, a change in the slope of the plot of  $RT \ln(k_{el})$  vs.  $\Delta G_{el}$  may occur.<sup>29,32</sup>

(32) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, 103, 3370–3378.

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small in fluid solution, we were unable to observe sensitized emission,<sup>48</sup> but several lines of evidence argue for an energy-transfer component to the quenching.

First, energy transfer certainly occurs at some rate since it is energetically feasible. While population of the quartet states may not be favorable, the data in Table II show that energy transfer from  $^*Cu(dpp)_2^+$  to the doublet states is a downhill process in every case. In fact, quenching rate constants of  $10^7$ – $10^8$   $M^{-1} s^{-1}$  are typical of energy-transfer reactions involving Cr(III) systems.<sup>3,50</sup> That the  $k_q$  values are roughly constant in the region where electron-transfer quenching is endergonic is also consonant with energy-transfer quenching. This follows because the energies of the acceptor levels and the reorganizational energies—two important factors determining energy-transfer rates<sup>52</sup>—are very similar throughout the series. The data in Table II show that the zero-zero energies of the doublet states span a narrow range, and, as is well-known, the population of these states requires minimal structural reorganization. For energetic reasons the quartet states are less likely to be involved in the quenching, but it is worth noting that the vertical excitation energies of these states are all very similar as well. Also in keeping with our hypothesis, energy-transfer quenching is expected to plateau at a much lower rate than electron-transfer quenching. This is because energy transfer to d-d excited states generally occurs by a collisional (or exchange) mechanism which, by comparison with that of electron transfer, has rather exacting requirements for overlap among donor and acceptor orbitals.<sup>52-54</sup> As a final piece of supporting evidence, we note that when energy transfer is supposed to dominate, the quenching rates vary inversely with the nephelauxetic parameter  $\beta$  (Table II). Two separate studies have found this to be typical of energy-transfer processes involving Cr(III) complexes.<sup>54,55</sup> More specifically, it has been proposed that the rate constant for energy transfer is proportional to the quantity  $(1 - \beta^{1/2})^2$ .

Since electron-transfer and energy-transfer quenchings occur as parallel processes for the Cr(III) series, we have fit the results to eq 7.  $k_{el}$  is calculated as before, using the previously determined value of  $k_{**}$ . The weighted, least-squares fit of the data occurs

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{el} + k_{en}^{\circ} (1 - \beta^{1/2})^2} \quad (7)$$

with  $k_{en}^{\circ} = 1 \times 10^9$   $M^{-1} s^{-1}$  and  $k_{QQ} = 2 \times 10^9$   $M^{-1} s^{-1}$ . In reality each complex exhibits a unique set of rate constants; our estimates should be regarded as representative, or average, values which are useful for relating the quenching results to other kinetic data.

Few self-exchange constants have been reported for Cr(III)/Cr(II) couples, and the available data pertain to aqueous solution. Published values are  $1.1 \times 10^8$   $M^{-1} s^{-1}$  for Cr(bpy)<sub>3</sub><sup>3+/2+</sup>,<sup>56</sup>  $3 \times 10^3$   $M^{-1} s^{-1}$  for Cr(EDTA)<sup>1-/2-</sup>,<sup>57</sup> and  $<10^{-5}$   $M^{-1} s^{-1}$  for the aquo couple.<sup>58,59</sup> Of these, only the bipyridine system involves the low-spin form of Cr(II), and it exhibits by far the largest rate

constant for the self-exchange reaction. As pointed out by Zwickel and Taube,<sup>60</sup> minimal structural reorganization occurs in this case because formation of the reduced complex does not require the population of a metal-ligand  $\sigma$  antibonding orbital. On the basis of our estimate of  $k_{QQ}$ , we infer that those derivatives of Cr(acac)<sub>3</sub> which quench by the electron-transfer mechanism also exhibit a low-spin Cr(II) ground state, although the possibility that the low-spin form represents a low-lying excited state is not excluded. Incidentally, determining the spin of these Cr(II) complexes is actually a novel use of our excited-state reagent since the Cr(acac)<sub>3</sub><sup>-</sup> systems themselves have, to our knowledge, never been isolated. (The Cr(acac)<sub>2</sub> forms are the known compounds.) The formation of low-spin Cr(II) may seem somewhat surprising since the isoelectronic complex Mn(acac)<sub>3</sub> is reported to be high spin.<sup>61</sup> However, d- $\pi^*$  back-bonding is likely to be more significant in the Cr(II) complexes, especially when the polyfluorinated ligands are involved, as electron-withdrawing substituents would be expected to enhance the  $\pi$ -acid character of the ligand. The presence of significant back-bonding would enhance the ligand field splitting and would encourage the formation of the low-spin complex.

As regards the resolved energy-transfer rates, we have already noted that their magnitudes are consistent with previous reports in the literature. However, the relationship between the energy-transfer rates and the nephelauxetic effect deserves further comment. In the ligand field model  $\beta$  is defined as the ratio of  $B$ , the effective Racah parameter of the complex, to that of the free ion ( $B_0 = 0.128$  V), where the Racah parameter describes part of the interelectron repulsion energy of the d electrons.<sup>62</sup> In the free ion, Cr<sup>3+</sup>, the energy of the doublet level is  $9B + 3C$  with respect to the ground state, where  $C$  is another Racah parameter.<sup>62</sup> With the common assumption that  $C \approx 4B$ , the energy of the doublet state is approximately given by  $21B$ .<sup>63</sup> In general the doublet state occurs at lower energy in a complex than it does in the free ion, and  $\beta$  is less than 1. Therefore, as  $\beta$  decreases, the driving force for energy transfer increases; however, this is probably not the reason for the inverse correlation between  $k_q$  and  $\beta$ . Maestri and Sandrini examined the temperature dependence of energy-transfer reactions involving a number of Cr(III) systems, and they found that the activation energy for quenching was small in all cases and that it actually increased with the driving force for the reaction.<sup>55</sup> They suggested that the nephelauxetic effect influences another factor in the expression for the energy-transfer rate constant, namely the transmission coefficient.<sup>52</sup> The effect arises because the ligands about the chromium center tend to shield the d orbitals, thereby restricting overlap with the orbitals of the quencher and reducing the magnitude of the transmission coefficient. Although a complex balance of factors are involved in determining the magnitude of  $\beta$ ,<sup>62,64</sup> smaller values of  $\beta$  are usually ascribed to increased covalency in the metal-ligand bonding. To the extent that it occurs, the admixture of ligand-centered orbitals with the  $t_{2g}$  orbitals of Cr(III) would be expected to facilitate overlap with the orbitals of the quencher, to promote energy transfer, and to lead to an inverse correlation between  $\beta$  and  $k_q$ . Steric effects may also affect the overlap and influence the rate of energy transfer,<sup>65</sup> however, the molecular size does not vary dramatically or in any systematic way across the acac series.

## Conclusions

The charge-transfer excited state of  $Cu(dpp)_2^+$  is a potent reductant which undergoes facile electron transfer, as has been shown by quenching studies with a series of nitroaromatics and a series of Cr(acac)<sub>3</sub> derivatives. In  $CH_2Cl_2$  the self-exchange rate involving  $Cu(dpp)_2^{2+}$  and  $^*Cu(dpp)_2^+$  is about  $8 \times 10^9$   $M^{-1}$

(48) Sensitized emission has been reported from Cr(acac)<sub>3</sub> in a viscous solution at low temperature; however, it was necessary to use very long-lived excited-state donors.<sup>49</sup>

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s<sup>-1</sup>, in accord with the fact that the exchanging electron is located in the  $\pi$  system of the aromatic ligand. The Cr(III) quenchers span a wide range of electrode potential and can be expected to be useful in other quenching studies, especially if the excited-state reduction potential is quite negative. The quenching results for the Cr(III) series are somewhat complicated because parallel energy-transfer and electron-transfer quenching occurs. Fortunately, because (exergonic) electron-transfer quenching enjoys a considerable kinetic advantage and because the rate constant for energy-transfer quenching is nearly constant across the series, the analysis of the rate data is straightforward. Apparently, low-spin Cr(II) products are formed when electron-transfer

quenching occurs, minimizing the overall activation energy of the process.

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**Registry No.** Cu(dpp)<sub>2</sub><sup>+</sup>, 85626-37-5; Cr(hFac)<sub>3</sub>, 14592-80-4; Cr(hFac)(tFbzac)<sub>2</sub>, 94620-39-0; Cr(tFbzac)<sub>3</sub>, 28096-65-3; Cr(tta)<sub>3</sub>, 15488-08-1; Cr(tFac)<sub>3</sub>, 14592-89-3; Cr(dbm)<sub>3</sub>, 21679-35-6; Cr(pdo)<sub>3</sub>, 15636-02-9; *cis*-Cr(bzac)<sub>3</sub>, 64726-51-8; *trans*-Cr(bzac)<sub>3</sub>, 64726-50-7; Cr(acac)<sub>3</sub>, 21679-31-2; *p*-dinitrobenzene, 100-25-4; *m*-dinitrobenzene, 99-65-0; 4,4-dinitrobiphenyl, 1528-74-1; 1-chloro-4-nitrobenzene, 100-00-5; nitrobenzene, 98-95-3.

## Modes of Rearrangements in *cis*-M(AB)<sub>2</sub>XY Six-Coordinate Bis Chelate Complexes. 1. A Theoretical Study of the Possibilities of 1D and 2D NMR

Rudolph Willem,<sup>\*1a</sup> Marcel Gielen,<sup>1a</sup> Henri Pepermans,<sup>1a,2</sup> Jean Brocas,<sup>1b</sup> Daniel Fastenakel,<sup>1b</sup> and Paolo Finocchiaro<sup>1c</sup>

Contribution from the Vrije Universiteit Brussel AOSC-TW, B-1050 Brussel, Belgium, the Université Libre de Bruxelles, Service de Chimie Organique et Collectif de Chimie Organique Physique, B-1050 Bruxelles, Belgium, and the Faculty of Engineering, University of Catania, I-6-95125 Catania, Italy. Received May 10, 1984

**Abstract:** This work presents a detailed permutational analysis of isomerism and rearrangements of *cis* bis chelate complexes of the type M(AB)<sub>2</sub>XY. This analysis establishes the full correlation between the modes of rearrangements of M(AB)<sub>2</sub>XY systems and those of the M(AA)<sub>2</sub>X<sub>2</sub>, M(AB)<sub>2</sub>X<sub>2</sub>, and M(AA)<sub>2</sub>XY systems previously described, through the concept of mode splitting. The low symmetry of M(AB)<sub>2</sub>XY systems results in a larger number of modes, allowing one to distinguish all rearrangements, provided signal assignments are possible. It is demonstrated that even in the absence of signal assignment use of 2D NMR spectroscopy gives the number of modes of rearrangements and the type of exchange pattern responsible for observed isomerizations in the M(AB)<sub>2</sub>XY systems, types of stereochemical information hard to deduce from the traditional analysis of residual diastereotopism in the fast exchange region of 1D spectra. The merits of both 1D and 2D NMR spectroscopy are discussed in light of the dynamic stereochemistry of M(AB)<sub>2</sub>XY systems.

Twenty years of intensive research have been performed on the dynamic stereochemistry of six-coordinate bis chelate complexes.<sup>3</sup> Several theoretical descriptions have been given for the rearrangements of systems of the types *cis*-M(AA)<sub>2</sub>X<sub>2</sub>, *cis*-M(AB)<sub>2</sub>X<sub>2</sub>, and *cis*-M(AA)<sub>2</sub>XY in which X and Y represent monodentate ligands and AA represents symmetric and AB dissymmetric bidentate ligands.<sup>4</sup> In contrast, M(AB)<sub>2</sub>XY systems were described

only shortly.<sup>4e,f</sup> It is the first aim of this paper to give a unifying description of the four systems based on the concept of modes of rearrangements, and especially, of mode splitting. Special emphasis will be put on the permutational analysis of the dynamic stereochemistry of M(AB)<sub>2</sub>XY systems. Systems with two different chelates do not need to be discussed since they do not provide additional dynamic stereochemical information, the number of observable modes being already maximum for M(AB)<sub>2</sub>XY.

Residual diastereotopism<sup>6,7</sup> in the fast exchange region of a 1D (one-dimensional) NMR spectrum only seldom gives direct information on the number of modes of rearrangements which determine this stereochemical conversion: when only low, and,

(1) (a) Vrije Universiteit Brussel. (b) Université Libre de Bruxelles. (c) University of Catania.

(2) Aspirant at the Belgian Nationaal Fonds voor Wetenschappelijk Onderzoek (NFWO).

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