(101) G. N. Schrauzer and L.-P. Lee, *J. Am. Chem. Soc.*, **90**, 6541 (1968).
(102) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
(103) B. J. Kalbacher and R. D. Bereman, *Inorg. Chem.*, **12**, 2997 (1973).
(104) Y. Nishida and S. Kida, *Chem. Lett.*, 57 (1973).
(105) A. von Zelewsky and H. Fierz, *Helv. Chim. Acta*, **56**, 977 (1973).
(106) K. Migita, M. Iwaizumi, and T. Isobe, *J. Am. Chem. Soc.*, **97**, 4228 (1975).
(107) E. Ochiai, *J. Chem. Soc., Chem. Commun.*, 489 (1972).
(108) C. J. Hipp and W. A. Baker, *J. Am. Chem. Soc.*, **92**, 792 (1970).
(109) See for instance the references quoted in M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(110) P. Fantucci, V. Valenti, F. Cariati, and I. Fragala, *Inorg. Nucl. Chem. Lett.*, **11**, 585 (1975).
(111) A similar situation where the lowest ionization potential does not correspond to the open-shell orbital for a system with one unpaired electron has been reported previously for the ion $CuCl_4^{2-}$[112]
(112) J. Demuynck, A. Veillard, and U. Wahlgren, *J. Am. Chem. Soc.*, **95**, 5563 (1973).
(113) M.-M. Coutière, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, **27**, 281 (1972).
(114) M.-M. Rohmer and A. Veillard, *J. Chem. Soc., Chem. Commun.*, 250 (1973).
(115) M.-M. Rohmer, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, **36**, 93 (1974).
(116) S. Evans, M. F. Guest, I. H. Hillier, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **70**, 417 (1974).
(117) W. van der Lugt, *Int. J. Quantum Chem.*, **6**, 859 (1972).
(118) We refer the reader to the work of Hoffmann et al. on the coordination of the nitrosyl ligand for a detailed discussion of the interactions between a metal atom and a diatomic ligand in a linear or bent structure.[119]
(119) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, and D. M. P. Mingos, *Inorg. Chem.*, **13**, 2666 (1974).
(120) A qualitative discussion of the interactions between the metal 3d and the dioxygen $\pi_g{}^a$ and $\pi_g{}^b$ orbitals has been given by Ochiai.[121]
(121) E. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 3375 (1973).
(122) A. Dedieu and A. Veillard, *Theor. Chim. Acta*, **36**, 231 (1975).
(123) Ochiai assigned the unpaired electron to the $\pi_g{}^b$ orbital but no rationale was given for this assignment.[121]
(124) We have already mentioned[122] that a limited configuration interaction between the three S configurations does not change this conclusion.[131]
(125) Obviously the use of the notation $\pi_g{}^a$ and $\pi_g{}^b$ to label the molecular orbitals of the dioxygen complex does not imply that these orbitals are pure ligand orbitals (see Figure 8 for the mixing of $\pi_g{}^a$ and d_{z^2}).
(126) M.-M. Rohmer, A. Dedieu, and A. Veillard, *Theor. Chim. Acta*, **39**, 189 (1975).
(127) An independent SCF calculation for the oxygen molecule yields orbital energies of -0.697 and -0.720 au for the $3\sigma_g$ and $1\pi_u$ orbitals, the antibonding orbital $1\pi_g$ being at higher energy.
(128) According to perturbation theory, the degree of interaction between two orbitals depends both on their overlap and on the corresponding energy gap denominator.[129]
(129) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).
(130) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955).
(131) A. Dedieu, Thèse de Doctorat d'Etat, Strasbourg, 1975.
(132) T. Koopmans, *Physica* (*Utrecht*), **1**, 104 (1933).
(133) Koopmans' theorem is easily extended to the open-shell orbital in the Restricted Hartree–Fock formalism of Roothaan[82] with two hamiltonians. Although Koopmans' theorem is not appropriate to discuss the sequence of ionization energies for a given molecule, it is probably safe for discussing the change in the ionization potential associated with a given MO within a series of related molecules.
(134) M. J. Carter, L. M. Engelhardt, D. P. Rillema, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 810 (1973).
(135) The energy associated with the $(d_{z^2})^2$ configuration is much higher at -2013.121 au for L = none.
(136) Preliminary calculations for the $Fe^{II}(porphyrin)O_2$ system, similar to the ones reported here, yield the $(\pi_g{}^a)^2$ configuration for the ground state of the bent structure and the $(\pi_g{}^b)^2$ configuration for the perpendicular structure. This latter one is found less stable than the bent one by about 63 kcal/mol.[137]
(137) A. Dedieu, M.-M. Rohmer, M. Benard, and A. Veillard, *J. Am. Chem. Soc.*, **98**, 3717 (1976).
(138) G. Herzberg, "Spectra of Diatomic Molecules", Van Nostrand, New York, N.Y., 1950.
(139) A referee has objected that these calculations have no bearing on reality (with respect to the ease of oxygenation) since only the case L = imidazole shows experimentally an appreciable tendancy to bind O_2 reversibly, and furthermore the Co(acacen) system does not even bind CO. Our calculation does indicate little binding of CO to Co(acacen) (the computed enthalpy being 1 kcal/mol, see Table 1 of ref 122). The aim of such calculations, which should be considered as model calculations, is not to compute the enthalpies of oxygenation to within a few kcal/mol, but rather to account for some general trends (such as the stabilizing effect of the fifth ligand for the adduct or the relationship between the ease of oxygenation and the ease of oxidation of the metal). Ligands such as CN^- or CO were not considered per se but rather respectively as a model for a good σ donor and poor π acceptor or a poor σ donor and good π acceptor.

Luminescence Quenching of the Tris(2,2′-bipyridine)ruthenium(II) and Tris(1,10-phenanthroline)ruthenium(II) Cations

J. N. Demas* and J. W. Addington

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901.

Received September 16, 1975

Abstract: Luminescence quenching of the tris(2,2′-bipyridine)ruthenium(II) and tris(1,10-phenanthroline)ruthenium(II) cations by over 20 metal complexes and ions is reported. Quenching is predominantly by diffusion, but a small contribution of static quenching is present for the anionic quenchers. Heavy atom and paramagnetic quenching are unimportant deactivation pathways, and all quenching appears to be by electron and energy transfer. A general method for estimating infinite dilution ion pairing and quenching constants from luminescence data is described. Infinite dilution bimolecular quenching constants, $k_2{}^0$'s, and ion pairing constants are reported. The Debye theory adequately describes the maximum permissible $k_2{}^0$'s, but may only predict variations of k_2 with ionic strength up to $I \sim 0.001$. Decay times and excited state energies are reported for both donors, and they are compared as sensitizers. Using these sensitizers the lowest excited triplet state of $Co(CN)_6{}^{3-}$ is estimated at ~ 18.4 kK $< E_t < \sim 20$ kK and for $Fe(CN)_6{}^{4-}$ it is suggested that $E_t < \sim 18.0$ kK.

Since its introduction as a photosensitizer,[1] the tris(2,2′-bipyridine)ruthenium(II) cation has proved revolutionary.[2-16] It functions as an energy and an excited-state electron-transfer agent in a variety of inorganic and organic systems. It forms the prototype of a class of sensitizers whose energies can almost continuously span the visible into the near infrared.[13] It has formed the basis of a chemical actinometer for high power lasers[14] and promises to be useful in solar energy conversion.[8] We present a comprehensive study of the quenching of $Ru(bipy)_3{}^{2+}$ and the related $Ru(phen)_3{}^{2+}$ [bipy = 2,2′-bipyridine and phen = 1,10-phenanthroline] by transition metal complexes.

Experimental Section

The acetylacetonates from Alfa Inorganics were recrystallized from benzene. The Co(III) and Cr(III) complexes were assumed to be anhydrous. Microanalysis showed the Cu complex to be anhydrous and the Co(II) and Ni(II) complexes analyzed to be dihydrates.

The $Cr(en)_3Cl_3{\cdot}3H_2O$ (en = ethylenediamine), $BaPt(CN)_4$, K_2PtCl_6, and $K_3Co(CN)_6$ from Alfa Inorganics were used without further purification. The $Co(NH_3)_6Cl_3$, $[CoCl(NH_3)_5]Cl_2$, $K_3Cr(CN)_6$, $K_3Co(C_2O_4)_3{\cdot}3H_2O$, $K_3Cr(C_2O_4)_3{\cdot}3H_2O$, and K_2PtCl_4 from Alfa were purified as follows: The $Co(NH_3)_6Cl_3$ was converted to the perchlorate by twice precipitating it with $HClO_4$. The $K_3Cr(CN)_6$ was repeatedly recrystallized from water to yield pale yellow crystals. The $K_3Cr(C_2O_4)_3{\cdot}3H_2O$ and $K_3Co(C_2O_4)_3{\cdot}3H_2O$ were precipitated from water with methanol. The K_2PtCl_4[17] and $[CoCl(NH_3)_5]Cl_2$[18] were purified by standard procedures. $K_2Ni(CN)_4$ was prepared by a standard procedure.[19] The remaining quenchers and chemicals were reagent grade and were used without further purification.

The $[Ru(bipy)_3]Cl_2{\cdot}6H_2O$ from G. F. Smith Chemical Co. was used without further purification; $[Ru(bipy)_3](ClO_4)_2$ was obtained by repeated precipitations with $HClO_4$. $[Ru(phen)_3](ClO_4)_2$ was obtained by oxalate reduction of $RuCl_3$ with 1,10-phenanthroline.[20] Emission and absorption spectra and τ's of both complexes agreed well with the literature values.

All luminescence measurements were carried out on an instrument constructed in our laboratory. Light from a 1000 W Hanovia mercury-xenon arc lamp was filtered through 5 cm of aqueous $CuSO_4{\cdot}5H_2O$ (100 g/l.) and focused into a 0.25 m Bausch and Lomb monochromator (6.6 nm/mm dispersion). An achromatic lens focused the excitation beam onto the sample. The emission monochromator, a scanning double-pass Perkin-Elmer Model 99 with a glass prism, had less than 0.4 kK/mm dispersion across the visible region.

The detector, an RCA C31034 photomultiplier, gave excellent sensitivity to beyond 850 nm and was usable to beyond 900 nm. The phototube signal was processed with a PAR 120 lock-in amplifier tuned to 13 Hz, the frequency of the monochromator's internal chopper. The amplifiers input resistance (10 MΩ) was the load resistor. To prevent phototube fatigue, the average phototube current was less than ~10 nA.

Monochromators were calibrated with discharge tubes to an accuracy of <1-1.5 nm. Emission spectra were not corrected. Low temperature (77 K) emission spectra of donors ($\sim 1\text{-}5 \times 10^{-5}$ M) were in ethanol-methanol (4/1 v/v) or methanol-water (4/1 v/v) glasses.

Quenching studies used square Pyrex cuvettes (~15 ml). All solutions were carefully deoxygenated with solvent-saturated ultra-pure nitrogen and measurements were made at ~21 °C.

Two quenching procedures were used. For some water soluble, poorer quenchers, solid quencher was added to the donor solution. In the other procedure a stock solution of the quencher was made up in the stock donor solution. After obtaining a reading with pure donor, ϕ_0, aliquots of this quencher solution were added with readings, ϕ's, between additions. Up to nine readings were obtained for light stable or weakly photosensitive systems. For highly photosensitive systems, a separate run was made for each datum point or very low excitation intensities were used.

Ionic strength studies used a fixed quencher concentration. After obtaining the ϕ_0 and ϕ, the ionic strength was varied by pipeting in aliquots of either KNO_3 or $KClO_4$ made up in a stock solution of donor and quencher, both at the same concentration as now in the cell. The initial ϕ_0/ϕ was ~3-5.

Data were corrected for trivial absorption of the exciting and emitted light by the quencher[3] to give corrected ratios, $(\phi_0/\phi)_{corr}$. Excitation and emission wavelengths were usually selected to minimize trivial corrections, with 408, 436, 460, and 480 nm excitation and 600 or 650 nm emission being used.

The decay time apparatus and the detailed measurement procedure are described elsewhere.[21] The decays were exponential over at least 2-3 half-lives. Reproducibility of mean lifetimes, τ, run in triplicate on the same sample were typically ~±1%. Reproducibility from day to day was <5%. Accuracy was probably better than 5%.

We estimate the errors in our quenching constants to be generally ~5-10%, although for substances with very low quenching constants or with large trivial effects errors are somewhat larger. For comparison of ϕ and τ data, the same stock solution was used for both measurements and the relative accuracy is typically better than 5%.

Results

The decay times in the absence of quencher, τ_0's, for $Ru(bipy)_3^{2+}$ in deoxygenated water and methanol (21 °C) were 0.600 and 0.765 μs, respectively. For $Ru(phen)_3^{2+}$ in deoxygenated water and methanol, τ_0's were 1.08 and 0.313 μs, respectively.

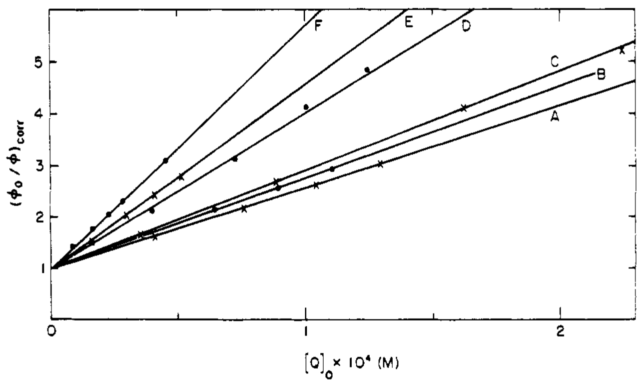

Figure 1. Intensity Stern–Volmer plots for quenching of $Ru(phen)_3^{2+}$ by: (A) $Cr(C_2O_4)_3^{3-}$; (B) $Cr(CN)_6^{3-}$; (C) $PtCl_4^{2-}$; (D) $Co(C_2O_4)_3^{3-}$; (E) $Fe(CN)_6^{3-}$; and (F) $Fe(CN)_6^{4-}$. All data are for water solutions.

For each of the two donors, the energy of the shortest wavelength emission maximum, E_{max}, and the energy at which this band's intensity falls to 5% of the peak on the short wavelength's side, $E_{5\%}$, are independent (≤0.1 kK) of the glass at 77 K. For $Ru(bipy)_3^{2+}$, $E_{max} = 17.2$ kK and $E_{5\%} = 18.0$ kK. For $Ru(phen)_3^{2+}$, $E_{max} = 17.7$ kK and $E_{5\%} = 18.4$ kK. Because of the band sharpness and the flat phototube response characteristics, these values should not be off by more than ±0.2 kK.

We define a Stern–Volmer quenching constant both for the decay time and the intensity measurements: $K_{sv}^{\tau} = [\tau_0/\tau - 1]/[Q]_0$ and $K_{sv}^{\phi} = [(\phi_0/\phi)_{corr} - 1]/[Q]_0$ where $[Q]_0$ is the formal added quencher concentration. Figure 1 shows typical intensity Stern–Volmer quenching plots. The decay time Stern–Volmer plots also appear linear and are not reproduced here.

Figures 2 and 3 show results with $Ru(bipy)_3^{2+}$ and $Ru(phen)_3^{2+}$ for a number of anionic quenchers. Only donor and quencher were present, and in these cases the K_{sv}^{τ} curves lie above the K_{sv}^{ϕ} curves; although in the cases with $K_3Cr(C_2O_4)_3$, the very small discrepancy might be caused by a systematic error. For a number of other complexes, Table I summarizes quenching results using the ϕ method which is considerably easier and, in the case of the very poor quenchers, more sensitive than the τ method.

Photosensitive systems are also indicated in Table I. Change of emission intensity with time (~1-2 min) certainly demonstrates a sensitized reaction; however, failure to detect a reaction does not necessarily preclude sensitivity.

We find no detectable quenching of $Ru(phen)_3^{2+}$ by $Cr(en)_3^{3+}$, of $Ru(bipy)_3^{2+}$ by $Co(NH_3)_6^{3+}$, Co^{2+}, and $BaPt(CN)_4$ or of either donor by $KClO_4$ and KNO_3. $Co(NH_3)_6^{3+}$ weakly quenches $Ru(phen)_3^{2+}$ with sensitized decomposition. Co^{2+} and possibly Ni^{2+} do appear to quench $Ru(phen)_3^{2+}$ very weakly but a small systematic error may be the cause. With I^-, $Co(CN)_6^{3-}$, and Ag^+, quenching is certainly present, but since as little as 0.01-0.1% of a highly quenching impurity could explain the data, the K_{sv}'s represent upper limits. In all other cases the quenching is certainly real and, we believe, due to the indicated compound and not to adventitious impurities.

Using the τ method we have checked quenching of $Ru(bipy)_3^{2+}$ by $AgNO_3$ and $K_3Co(CN)_6$. Within ~20%, experimental uncertainty, we find K_{sv}^{ϕ} and K_{sv}^{τ} to be the same.

We have also compared K_{sv}^{ϕ} and K_{sv}^{τ} for Cu^{2+} quenching of $Ru(bipy)_3^{2+}$ at fixed $[Cu^{2+}]$ while adding KNO_3 (Figure 4). Again there is a small difference between the two data sets.

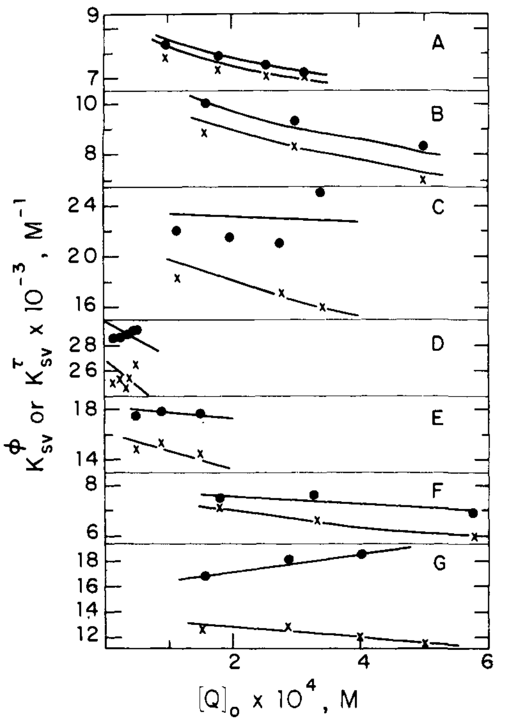

Figure 2. K_{sv}^{ϕ} (●) and K_{sv}^{τ} (×) quenching of $Ru(bipy)_3^{2+}$ by: (A) $Cr(C_2O_4)_3^{3-}$, (B) $Cr(CN)_6^{3-}$, (C) $Fe(CN)_6^{3-}$, (D) $Fe(CN)_6^{4-}$, (E) $Co(C_2O_4)_3^{3-}$, (F) $PtCl_4^{2-}$, and (G) $Ni(CN)_4^{2-}$. The upper and lower lines for each part are the calculated best-fit K_{sv}^{ϕ} and K_{sv}^{τ} curves, respectively; parameters are given in Tables I and II.

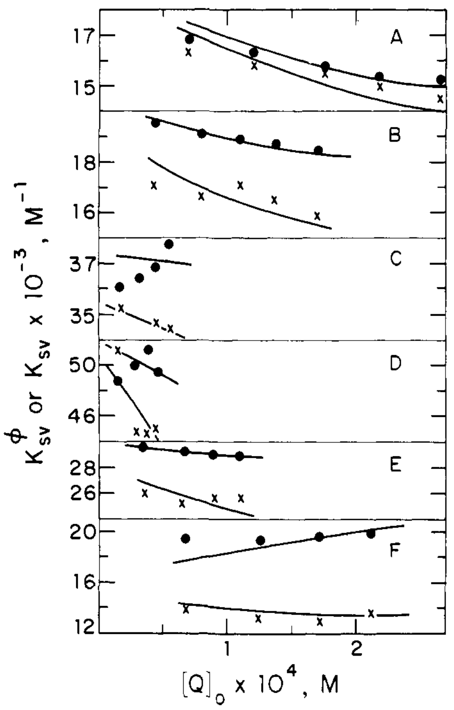

Figure 3. K_{sv}^{ϕ} (●) and K_{sv}^{τ} (×) for quenching of $Ru(phen)_3^{2+}$ by: (A) $Cr(C_2O_4)_3^{3-}$, (B) $Cr(CN)_6^{3-}$, (C) $Fe(CN)_6^{3-}$, (D) $Fe(CN)_6^{4-}$, (E) $Co(C_2O_4)_3^{3-}$, and (F) $PtCl_4^{2-}$. The upper and lower lines are calculated best-fit K_{sv}^{ϕ} and K_{sv}^{τ} curves, respectively; parameters are given in Tables I and II.

Trivial corrections are significant, however, and experimental error may explain the discrepancies.

Additional ionic strength effects were carried out with $Ru(bipy)_3^{2+}$ and $Ni(CN)_4^{2-}$ and $Fe(CN)_6^{4-}$. For $Fe(CN)_6^{4-}$ (9×10^{-5} M) there was no discernible difference (≤3%) between K_{sv}^{ϕ} vs. ionic strength, I, varying I with either KNO_3 or $KClO_4$ (1.6-3.6×10^{-2} M); with KNO_3, the log K_{sv}^{ϕ} vs. $1.02I^{1/2}/(1 + 2I^{1/2})$ plot[22] (0.03-0.10) was reasonably linear with a slope of ∼−6. Against the same scale, log K_{sv}^{τ} yielded a slope of ca. −(5-6) for the range 0.015-0.030. For $Ni(CN)_4^{2-}$ with KNO_3, the log K_{sv}^{ϕ} plot was linear with a slope of ca. −4 from 0.02-0.06, but the log K_{sv}^{τ} plot yielded a linear plot with a slope of ca. −2.6 over the 0.02-0.12 range without noticeable curvature. Without added KNO_3 (i.e., just varying $Ni(CN)_4^{2-}$), the log K_{sv} plot had a slope of ca. −3.5.

In the $Ru(bipy)_3^{2+}$-$Fe(CN)_6^{4-}$ system, ion pairing was tested for spectrally ($[Fe(CN)_6^{4}] \sim 5 \times 10^{-3}$ M). Binary solutions yielded spectra which were additive in the 400-460 nm donor's CT region but did show a very slight increase in absorbance for λ ≥470 nm.

Discussion

Luminescence quenching can be by two basic mechanisms: (1) normal diffusional or dynamic quenching of the Stern-Volmer type; (2) associational or static quenching where the donor and quencher form a nonluminescent association pair which reduces the amount of excitation energy absorbed by potentially luminescent donors.[9,15]

For a system exhibiting both processes eq 1 and 2 apply.[9,23]

$$K_{sv}^{\tau} = \frac{\tau_0/\tau - 1}{[Q]_0} = K_{sv}\frac{[Q]}{[Q]_0} \qquad (1)$$

$$K_{sv}^{\phi} = \frac{\phi_0/\phi - 1}{[Q]_0} = (\beta K_{eq} + K_{sv})\frac{[Q]}{[Q]_0} + \beta K_{eq}K_{sv}\frac{[Q]^2}{[Q]_0} \qquad (2)$$

$[Q]_0$ is the formal added concentration of quencher Q, [Q] is the concentration of free Q (i.e., nonassociated), K_{eq} is the association constant for donor with quencher, and K_{sv} is the true Stern-Volmer quenching constant for quenching of *D by Q and equals $k_2\tau_0$ where k_2 is the bimolecular quenching constant. β varies from 1.000 to ϵ_{DQ}/ϵ_D for optically dilute to dense solutions.[15,23] It is assumed that the association pair, DQ, does not significantly quench *D compared to free Q. These equations reduce to a very simple form when $[Q]_0 \gg [D]_0$ and have been used for estimating association constants.[15,16] In contrast to the previous results our experiments with charged species were not done under conditions of constant ionic strength or with $[Q]_0 \gg [D]_0$, and a more general treatment was required.

Equations 1 and 2 show that only if associational quenching is absent (i.e., $\beta K_{eq} = 0$) are the K_{sv}^{τ} and K_{sv}^{ϕ} vs. $[Q]_0$ curves identical. Thus, the differences between K_{sv}^{ϕ} and K_{sv}^{τ} of

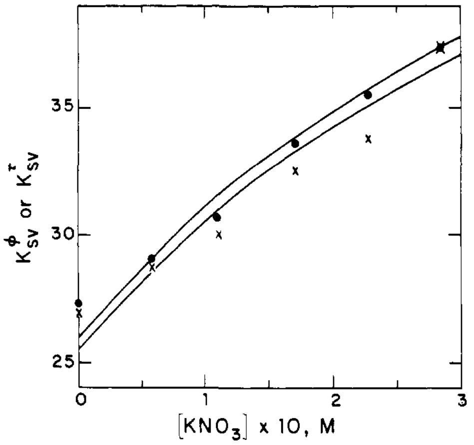

Figure 4. Variation of K_{sv}^{ϕ} (●) or K_{sv}^{τ} (×) with added KNO_3 for quenching of $Ru(bipy)_3^{2+}$ by Cu^{2+}. The upper and lower curves are the calculated best fit K_{sv}^{ϕ} and K_{sv}^{τ} curves, respectively, using $K_{eq}^0 = 0.3\ M^{-1}$, $K_{sv}^0 = 4.5\ M^{-1}$, and $\alpha = 3$.

Table I. Luminescence Quenching Data at ~21 °C

	$Ru(bipy)_3^{2+}$ [a,b]			$Ru(phen)_3^{2+}$ [a,c]			Theoretical
Quencher	K_{sv}^{ϕ}, M^{-1}	K_{sv}^0, M^{-1}	$k_2^0 \times 10^{-9}$, $M^{-1}\,s^{-1}$	K_{sv}^{ϕ}, M^{-1}	K_{sv}^0, M^{-1}	$k_2^0 \times 10^{-9}$, $M^{1}\,s^{-1}$	$k_2^0 \times 10^{-9}$, $M^{-1}\,s^{-1}$
$Co(NH_3)_6(ClO_4)_3$	0.5 ± 13 (2-9 × 10^{-3})	<2	<0.003	11 ± 4 (2-5 × 10^{-3})[d]	2.8 ± 1.0	~0.003	0.012
$Cr(en)_3Cl_3$				−4 ± 3 (3-7 × 10^{-3})	<1	<0.001	
$CoCl(NH_3)_5Cl_2$	103 ± 44 (2-5 × 10^{-3})[d]	43 ± 3	0.072	230 ± 30 (1-4 × 10^{-3})[d]	141 ± 3	0.131	0.13
$CoCl_2$	−2 ± 1 (5-7 × 10^{-2})	<0.3	<0.0005	1.4 ± 1 (5-6 × 10^{-2})	0.26 ± 0.2	0.000 2	
$CuSO_4$	22 ± 4 (5-6 × 10^{-2})	4.0 ± 0.5	0.006 6	50 ± 4 (3-6 × 10^{-2})	9.4 ± 0.8	0.009	
$NiSO_4$	1.9 ± 0.7 (5-7 × 10^{-2})	0.35 ± 0.16	0.000 6	4.1 ± 0.5 (5-6 × 10^{-2})	0.72 ± 0.04	0.000 66	
$AgNO_3$	1.4 ± 0.1 (0.5-1.2)[e]	0.40 ± 0.03	0.000 67	0.37 ± 0.03 (0.6-1.3)	0.081 ± 0.005	0.000 075	1.2
$Ni(acac)_2$	21 ± 2 (1-7 × 10^{-3})	21	0.027	13 ± 2 (2-7 × 10^{-3})	13	0.042	11
$Co(acac)_3$	430 ± 80 (1-10 × 10^{-3})	430	0.56	270 ± 30 (1-5 × 10^{-3})	270	0.86	
$Co(acac)_2$	44 ± 3 (2-8 × 10^{-3})	44	0.058	37 ± 6 (1-8 × 10^{-3})	37	0.12	
$Cr(acac)_3$	230 ± 4 (1-4 × 10^{-3})	230	0.30	170 ± 20 (1-4 × 10^{-3})	170	0.54	
$Cu(acac)_2$	840 ± 20 (3-12 × 10^{-4})	840	1.1	510 ± 30 (3-12 × 10^{-4})	510	1.6	
$KClO_4$	<0.3 (0.04)	<0.6	<0.001	<0.3 (0.04)	<0.6	<0.000 3	19
KNO_3	<0.1 (0.1)	<0.24	<0.000 4	<0.1 (0.1)	<0.24	<0.000 1	
NaI	0.10 ± 0.06 (0.5-0.7)	0.4 ± 0.2	0.001	0.34 ± 0.02 (0.14-0.16)	1.0 ± 0.2	0.001	
K_2PtCl_4	*f, d*	9100	15	*f, d*	18 200	17	36
K_2PtCl_6	17 000 ± 3000 (4-13 × 10^{-5})[d]	20 000 ± 4 000	34	21 000 ± 3 000 (1-3 × 10^{-4})[d]	26 000 ± 1 000	~24	
$BaPt(CN)_4$	<10 (6-17 × 10^{-3})	<40	<0.07	ppt			
$K_2Ni(CN)_4$	*f*	17 000	28	ppt			
$Na_3Co(NO_2)_6$	2500 ± 300 (2-7 × 10^{-4})[d]	5 200 ± 800	~9	ppt			54
$K_3Co(C_2O_4)_3$	*d, f*	22 800	38	*d, f*	38 100	35	
$K_3Co(CN)_6$	0.78 ± 0.17 (0.17)	19 ± 3	0.032	0.99 ± 0.18 (0.21)	29 ± 3	0.027	
$K_3Cr(C_2O_4)_3$	*f*	12 400	21	*f*	24 500	23	
$K_3Cr(CN)_6$	*f*	15 000	25	*f*	25 300	23	
$K_3Fe(CN)_6$	*f*	30 500	51	*f*	48 000	44	
$K_4Fe(CN)_6$	*f*	44 100	73	*f*	78 500	73	72

[a] Quencher concentration range, M, in parentheses. [b] Donor concentration 4.0 × 10^{-5} M. [c] Donor concentration 3.8 × 10^{-5} M. [d] Photosensitive. [e] $Ru(bipy)_3(ClO_4)_2$ donor ~10^{-5} M. [f] See figures.

Figures 2 and 3 clearly demonstrate the presence of both dynamic and static quenching. With $Cr(C_2O_4)_3^{3-}$ and Cu^{2+} (Figure 4), the discrepancies may be within experimental error, but we believe a limited amount of static quenching is probably present (~3-5%). It is particularly noteworthy that both processes can be present even when the intensity Stern-Volmer plots (Figure 1) appear linear. It is thus essential to combine both ϕ and τ data to obtain a complete description of the quenching paths.

It is possible to evaluate K_{sv} and βK_{eq} pointwise from pairs of K_{sv}^{τ} and K_{sv}^{ϕ} data and eq 1 and 2. Of more fundamental interest, however, are K_{sv}^0 and K_{eq}^0, the Stern-Volmer quenching constant and the equilibrium constant at $I = 0$. The following procedure obtained a K_{sv}^0 and K_{eq}^0 which gave a best fit to all data and accounted for the variations of K_{sv} and K_{eq} with I.

K_{eq} and K_{sv} were assumed to obey eq 3 and 4, respectively.

$$\log K_{eq} = \log K_{eq}^0 + z_1 z_2 F \qquad F = 1.02 I^{1/2}/(1 + 2I^{1/2}) \tag{3}$$

$$\log K_{sv} = \log K_{sv}^0 + z_1 z_2 F \qquad F = 1.02 I^{1/2}/(1 + \alpha I^{1/2}) \tag{4}$$

z_1 and z_2 are the units of electronic charge on the donor and acceptor and α is a system dependent parameter.

Equations 3 and 4 are the normal expressions for ionic equilibria and rates in aqueous solutions at room temperature.[24] Equation 3 uses $1 + 2I^{1/2}$ rather than the usual $1 + I^{1/2}$ to account for the larger size of our complex ions; our results, however, are very insensitive to the form of this term. In the Brönsted-Bjerrum treatment of rates, α is ($3.3 \times 10^7 a$) where "a" is the average effective diameter of the ions in ångströms.[24] More commonly, however, α is an adjustable parameter used to fit the data at higher ionic strengths.

Our treatment assumed $\beta = 1$ because of the small effect of ion pairing on visible absorption spectra and because the optical densities of our solutions were low (≤~0.5). Also only 1:1 ion pairs were assumed present.

An iterative grid-search least-squares method was used for determining K_{sv}^0 and K_{eq}^0. For a set of K_{sv}^{τ} and K_{sv}^{ϕ} data, a K_{sv}^0 and a K_{eq}^0 were guessed; then using eq 1-4 the expected K_{sv}^{τ}'s and K_{sv}^{ϕ}'s were computed. K_{sv}^0 and K_{eq}^0 were varied systematically to minimize the sums of the squares of the difference between the observed and calculated points (see Figures 2 and 3). Starting with widely varying initial guesses the same results within our resolution (~2% in K_{sv}^0 and ~5% in K_{eq}^0) were always obtained. All I's were calculated by an iterative procedure which accounted for the variations in ionic

Table II. Ion Pairing Constants at 21 °C

Anion	$K_{eq}{}^0$, M^{-1} Ru(bipy)$_3{}^{2+}$	$K_{eq}{}^0$, M^{-1} Ru(phen)$_3{}^{2+}$
$PtCl_4{}^{2-}$	250	2300
$Ni(CN)_4{}^{2-}$	1600	
$Co(C_2O_4)_3{}^{3-}$	1900	1900
$Cr(C_2O_4)_3{}^{3-}$	200	300
$Cr(CN)_6{}^{3-}$	400	500
$Fe(CN)_6{}^{3-}$	2000	1900
$Fe(CN)_6{}^{4-}$	3600	2800

species present. I was first calculated assuming the absence of ion pairing. K_{eq} was then estimated using eq 3, and the composition of the solution was calculated including the ion pairs. I was then recomputed and the entire process was repeated until the I after a calculation was the same as before. Convergence was rapid, and five iterations were always sufficient.

For most anionic complexes we set $\alpha = 2$ for eq 4, since $\alpha = 2$ is valid for quenching of organics[22] and of Ru(bipy)$_3{}^{2+}$ by $Cr(CN)_6{}^{3-}$.[25] Due to the low concentrations, the final fit or best parameters are not very sensitive to α.

For I^-, $ClO_4{}^-$, $NO_3{}^-$, $Pt(CN)_4{}^{2-}$, $PtCl_6{}^{2-}$, $Co(NO_2)_6{}^{3-}$, and $Co(CN)_6{}^{3-}$ where quenching was small or the data were not very accurate because of large correction factors or high photosensitivity, no attempt was made to evaluate $K_{eq}{}^0$. $K_{sv}{}^0$ was estimated from eq 4 with $\alpha = 2$ and $K_{sv}{}^{\Phi}$'s in place of K_{sv}'s.

For the cationic quenchers except Cu^{2+}, association was assumed unimportant and $K_{sv}{}^0$ was estimated from eq 4 with $\alpha = 3$ and $K_{sv}{}^{\Phi}$'s in place of K_{sv}'s. The choice of $\alpha = 3$ was based on its success with some cationic Cr(III) complexes[25] and for Cu^{2+} with Ru(bipy)$_3{}^{2+}$ (see below).

For $CuSO_4$ with Ru(bipy)$_3{}^{2+}$ assuming combinational quenching and using the general procedure, we found the fit with $\alpha = 3$ to be far better than $\alpha = 2$ and somewhat better than $\alpha = 4$. For $\alpha = 3$, the best fit gave $K_{sv}{}^0 = 4.5$ M^{-1} and $K_{eq}{}^0 = 0.03$ M^{-1}. Finer resolution in α was not attempted. The best fit plots are shown in Figure 4.

Table I summarizes the $K_{sv}{}^0$'s and the zero ionic strength bimolecular quenching constants, $k_2{}^0$, calculated from $k_2{}^0 = K_{sv}{}^0/\tau_0$. Theoretical $k_2{}^0$'s calculated from the Debye equation[26] with $(R_1 + R_2)/2 = 5A$ are included for comparison. Table II summarizes the calculated $K_{eq}{}^0$'s. Figures 2, 3, and 4 show the calculated best-fit curves.

The assumption of insignificant quenching by DQ is supported on several grounds. The majority of Q was always present as free Q and any DQ formed should have a significantly lower k_2 than would Q because of charge factors. Further, when we recalculated several curves assuming DQ quenched with the same rate constant as Q, the quality of the fit was worse. A small quenching contribution of DQ is certainly present, but it did not significantly affect the $K_{sv}{}^0$ or $K_{eq}{}^0$ estimates.

Quenching Rates and Ionic Strength Effects. Table I reveals that with many quenchers, $k_2{}^0$'s are within a factor of 2 of the theoretical maximum. In several cases the observed values equal the theoretical, but not once does the observed value exceed the theoretical. We, therefore, conclude that the Debye theory, in spite of its approximations, satisfactorily predicts limiting $k_2{}^0$'s for these charged metal complexes. Further, for a number of systems, the quenching efficiency per encounter is $\geq\sim 0.5$.

The calculated fits to the quenching data of Figures 2-4 are remarkably good, probably within experimental error. We conclude that our procedure for estimating $K_{sv}{}^0$'s and $K_{eq}{}^0$'s is valid and that eq 3 and 4 hold for $I \leq \sim 5\text{-}10 \times 10^{-4}$ if no electrolytes except the donor and quencher are present.

On the other hand $Fe(CN)_6{}^{3-}$ and $Ni(CN)_4{}^{2-}$ with added KNO_3 or $KClO_4$ failed to conform to eq 4 or to be fit satisfactorily by the generalized calculations even at I's where eq 3 and 4 were believed to be good. A remotely possible reason for the problem could be formation of a remarkably stable ion pair with K^+. These disturbing results suggest that at the least, considerable care should be exercised in obtaining $K_{eq}{}^0$'s and $K_{sv}{}^0$'s from data run at high ionic strengths; the apparent simplification resulting from use of a constant ionic strength may indeed prove highly misleading when infinite dilution values are desired. We therefore recommend whenever possible the use of no additional electrolyte and the correction for the variations in I by eq 3 and 4.

In the case of $Fe(CN)_6{}^{4-}$, $K_{sv}{}^{\Phi}$ is invariant when the ionic strength was fixed with either $KClO_4$ or KNO_3. This strongly suggests that Ru(bipy)$_3{}^{2+}$ is not strongly ion paired with either $NO_3{}^-$ or $ClO_4{}^-$.

One of the most remarkable features of the data is the virtual invariance of $k_2{}^0$'s or $K_{eq}{}^0$'s on going from Ru(bipy)$_3{}^{2+}$ to Ru(phen)$_3{}^{2+}$ for a given charged quencher. With few exceptions these numbers are equal within experimental error. Thus, to a quencher the excited donors look virtually identical in spite of the more extended, organic phen vs. bipy ligand. The charge polarized solvent sheath may be responsible for this leveling effect. The similar $K_{eq}{}^0$'s are not too surprising; both complexes have similar sizes, and electrostatic forces probably control stability. Thus, it may be possible to estimate the $K_{eq}{}^0$'s for a quencher with a related series of donors by a single $K_{eq}{}^0$ determination, thus avoiding difficult and time-consuming measurements.

For the uncharged acetylacetonate quenchers, however, Ru(phen)$_3{}^{2+}$ is uniformly a better donor than Ru(bipy)$_3{}^{2+}$ as judged by k_2's. This may reflect the less organic nature of Ru(bipy)$_3{}^{2+}$ as viewed from outside with a resultant increase in tightness of the methanol solvent sphere and a greater resistance to close association with organiclike quenchers.

Sensitizer Characteristics. A key characteristic for interpretation of sensitizations is the donor's excited state energy. For assigning zero point energies of CT states we adopt the Fleischauer criterion[27] although it has not been confirmed as suitable for CT states. It is, however, easy to use and relatively insensitive to emissive impurities. Since spin labels are probably inappropriate for these CT states[28,29] we use E_0's to refer to the zero-point energy difference between the thermally equilibrated ground and excited states. The solvent-independent E_0's of Ru(phen)$_3{}^{2+}$ and of Ru(bipy)$_3{}^{2+}$ at 77 K are ~18.4 kK and ~18.0 kK, respectively. We infer that these values hold in methanol or water at room temperature. The bands are sharp, and errors in E_0's should not be large (<0.5 kK); 0.4 kK is usually insignificant, and either donor should be energetically equivalent.

Based on our K_{sv}'s Ru(phen)$_3{}^{2+}$ is clearly a superior sensitizer for exploratory work in aqueous solutions as long as insoluble double salts do not form. In methanol, however, Ru(bipy)$_3{}^{2+}$ is superior because of the higher K_{sv}'s and because it is commercially available at low cost.

In a practical sense, Ru(bipy)$_3{}^{2+}$ and Ru(phen)$_3{}^{2+}$ will probably only find wide usage with anionic quenchers because of the enormous charge dependence of $k_2{}^0$'s (Table I). New neutral and anionic sensitizers such as Ru(bipy)$_2$(CN)$_2$ and Ru(phen)$_2$(CN)$_2$[30] which frequently yield orders of magnitude improvements in K_{sv} will overcome these difficulties. Further, the neutral complexes are free of ion-pairing problems.

Ion Pairing. The ion-pairing constants of Table II appear reasonable.[31] There are no good data with which to compare our results. For the Ru(bipy)$_3{}^{2+}$-$Co(C_2O_4)_3$ system, intensity quenching methods used by Fujita and Kobayashi[32] lead to a

$K_{eq}^0 \sim 6000\ M^{-1}$ (by inference we assume $I = 0.04$), a value which is triple our estimate. The poor agreement probably arises out of their indirect method and failure to account for trivial effects. Indeed, it is unclear whether they saw static quenching at all. Our ability to see ion pairing of $Ru(bipy)_3^{2+}$ with $PtCl_4^{2-}$ and $Cr(CN)_6^{3-}$ in water while others[1,25] did not is almost certainly due to the greater accuracy of our τ measurements.

The apparent static quenching of $Ru(bipy)_3^{2+}$ by Cu^{2+}, if real, is not normal ion pairing although charge-transfer stabilization could be involved. More likely the apparent static quenching is nearest neighbor quenching; calculations ignoring repulsive energies are consistent with our data.[33]

Quenching Mechanisms. Possible bimolecular quenching mechanisms are (a) energy transfer, (b) excited donor-quencher chemical reaction,[5,34] (c) catalyzed deactivation without energy transfer or chemical reaction, and (d) exciplex formation. Our evidence seems to rule out all but energy transfer or chemical quenching in the current systems. The sensitized decomposition of $Co(NH_3)_6^{3+}$ with $Ru(phen)_3^{2+}$ as well as for $CoCl(NH_3)_5^{2+}$, $PtCl_4^{2-}$, $PtCl_6^{4-}$, $Co(NO_2)_6^{3-}$, and $Co(C_2O_4)_3^{3-}$ with both donors directly establishes some energy transfer or chemical quenching in these cases.

Excluding electron transfer, catalytic deactivation is probably a negligible quenching pathway. Catalytic effects are divided into two categories: (a) heavy atom quenching caused by an externally induced increase in the spin-orbit coupling,[35] and (b) quenching due to the high magnetic moment of the quencher.[36]

Persuasive arguments show that external heavy atom effects must be minimal in our systems. Our donors have an *internal* high atomic number atom ($Z = 44$ for Ru), and it is highly unlikely that *external* heavy atom quenchers, especially those with lower Z's (Co, Ni, Cr, Fe, and Cu), could have much effect. Experiments support this claim. I^- ($Z = 53$) and Ag^+ ($Z = 47$) quench exceedingly poorly or not at all; the k_2^0's are at least $\sim 10^3 - 10^4$ smaller than the theoretical limits. Platinum ($Z = 78$) complexes should be good quenchers, yet $Pt(CN)_4^{2-}$ is virtually a nonquencher. The quenching by $PtCl_4^{2-}$ and $PtCl_6^{2-}$ can be accounted for by electron or energy transfer, paths which are not available to $Pt(CN)_4^{2-}$ (see below). Therefore, heavy atom quenching of both donors makes at most a small contribution.

The magnetic moment hypothesis for quenching of triplet states is by no means established and indeed there are some reasons to doubt its validity for organics.[36] Only the Cr^{3+}, Co^{2+}, Cu^{2+}, and Fe^{3+} complexes and $Ni(acac)_2$, however, are paramagnetic and can quench by this route, but we rule out this pathway even for these species. If there were a correlation between magnetic moment and quenching ability, the k_2^0's for Co^{2+}, Ni^{2+}, Cu^{2+}, and $CoCl(NH_3)_5^{2+}$ would fall off monotonically. The observed order is probably the complete reverse with $CoCl(NH_3)_5^{2+}$ and Cu^{2+} being by far the better quenchers. For the acetylacetonato complexes, the behavior is not so extreme, but the paramagnetic $Co(acac)_2$ is an order of magnitude weaker quencher than the diamagnetic $Co(acac)_3$; of the paramagnetic substance of this group, $Cu(acac)_2$ with fewest unpaired electrons is definitely the best quencher. The diamagnetic $Ni(CN)_4^{2-}$ quenches on ~80% of the encounters but Ni^{2+} only ~0.5% and $Ni(acac)_2$ only ~0.3% of the time. Although some of these comparisons could be in error because of solvent or ligand effects, the consistent failure to find a correlation between magnetic moments and k_2^0's indicates that paramagnetic quenching is not a significant deactivation pathway.

Formation of a nonluminescent exciplex could account for our observed quenching, but we feel this possibility unlikely. Our donors are highly hindered toward formation of π complexes, a common form of exciplex in organics; the only known exciplexes involving transition metal complexes appear to be π complexes.[37] Most quenchers are also highly hindered. Thus, on steric grounds we rule out π complexes. A charge transfer stabilized exciplex is possible, but there is as yet no evidence for such species involving transition metal complexes.

The only type of exciplex which, we feel, bears serious consideration is one involving oppositely charged donors and acceptors, that is an ion pair where the donor is excited. Such a species while it should enhance the probability of energy or electron transfer because of the "sticky" collision is not in itself a viable mode of quenching. $Co(CN)_6^{3-}$, $Pt(CN)_4^{2-}$, and I^- must also form ion pairs with ground and excited donor, yet they do not quench appreciably. Therefore, ion pairing between an excited donor and quencher cannot itself quench; the alternate pathways of energy or electron transfer must also be present for quenching to occur.

Thus, quenching by energy transfer and donor-acceptor chemical reaction remain the most reasonable explanations. Energy transfer quenching of $Ru(bipy)_3^{2+}$ [1,4,9-12,14] is well documented. Electron transfer, the only reasonable chemical reaction, can occur by oxidation of $^*Ru(bipy)_3^{2+}$ to $Ru(bipy)_3^{3+}$ or by reduction to $Ru(bipy)_3^{+}$.[5-8] Our data are consistent with these processes.

As expected $KClO_4$ and KNO_3 do not quench, since they have no low-lying energy levels. All the other materials except I^-, $Pt(CN)_4^{2-}$, Ag^+, and possibly $Fe(CN)_6^{4-}$ and $Co(CN)_6^{3-}$ have energy levels which are lower than those of the donors and could thus quench by energy transfer. These facts can be confirmed from the absorption or emission spectra and by crystal field theory.

The lowest excited state of $Pt(CN)_4^{2-}$ at ~23 kK[27,38] is significantly higher than the donor level of $Ru(bipy)_3^{2+}$, thus the absence of any detectable quenching. The inability of $Pt(CN)_4^{2-}$ to quench $Ru(bipy)_3^{2+}$, however, is in striking contrast with the other d^8 square-planar complex $Ni(CN)_4^{2-}$, one of the best quenchers. The key difference between these species is that $Ni(CN)_4^{2-}$ has lower-lying levels than $Pt(CN)_4^{2-}$. For $Ni(CN)_4^{2-}$ we estimate $E_t \sim 18$ kK from absorption spectra[39] using the Fleischauer criterion.[27] This state, nearly isoenergetic with the donor levels, permits energy transfer; the very efficient quenching by $Ni(CN)_4^{2-}$ almost certainly confirms it. Electron transfer quenching of $Ni(CN)_4^{2-}$ has also been postulated, but the available electrochemical data do not support this claim.[5c]

The quenching of $Ru(bipy)_3^{2+}$ by $Fe(CN)_6^{3-}$ has been interpreted as arising solely from electron transfer from Ru(II)[5c] based on the incorrect assumption that energy transfer is impossible. The spectroscopy and crystal field calculation on $Fe(CN)_6^{3-}$ show its lowest excited state zero-point energy is well below 18 kK since the lowest visible absorption maximum is at 18.2 kK.[40] The absence of emission suggests levels even lower than this.

Quenching of $Ru(bipy)_3^{2+}$ and presumably $Ru(phen)_3^{2+}$ by $Fe(CN)_6^{4-}$ has been interpreted as occurring by electron transfer to $^*Ru(bipy)_3^{2+}$ since it is energetically feasible and the lowest visible absorption (presumably a $S \rightarrow T$) is well above 18 kK.[5c,d] Alternatively, we suggest that the lowest excited state of $Fe(CN)_6^{4-}$ may be well below 18 kK and just not visible in absorption which is common for spin-forbidden transitions. We base this on the absence of detectable visible or near-ir emission from $Fe(CN)_6^{4-}$ at 77 K either in a glass or in the solid state.[41] Also the formation of an apparently nonluminescent double salt with $Cr(en)_3^{3+}$ suggests the lowest state of $Fe(CN)_6^{4-}$ may be below the ~15 kK emitting doublet of $Cr(en)_3^{3+}$.

Except for $Co(acac)_3$, the sensitized photochemistry of the Co(III) complexes indicates at least some electron transfer quenching to yield Co(II),[7] although energy transfer is possible in all cases. The Cu(II) species can also presumably quench by electron transfer since reduction to Cu(I) should be easy. Failure to see decomposition with Cu(II) complexes and Co(acac)$_3$ could arise from back-electron transfer in the encounter complex or a fast bulk reaction.

Ag$^+$ is not likely to be a good electron transfer quencher since the reaction would be to a hydrated silver atom in solution. Estimates of the redox potential indicate little probability of this occurring which is consistent with the low rates.

Pt(III) intermediates are easily formed by the direct photolysis of PtCl$_6^{2-}$[42] and one-electron reduction to a reactive Pt(III) species by *Ru(bipy)$_3^{2+}$ and *Ru(phen)$_3^{2+}$ seems feasible. In view of the very high yield sensitized photochemistry of PtCl$_6^{2-}$, we suggest a large component of electron transfer quenching; energy transfer, however, is possible (E_0 $\sim$ 18 kK)[27,38] and both may occur. In the cases where both electron and energy transfer are possible, quantitative flash photolysis should permit determination of the rates of the energy and the electron transfer processes.

The remaining Ni^{2+}, Pt^{2+}, Co^{2+}, and Cr^{3+} complexes and Co(CN)$_6^{3-}$[5c] almost certainly cannot react by electron transfer, and we infer that quenching when present is by energy transfer. The failure to obtain good quenching in all cases no doubt represents variations in the detailed interaction terms on varying the ligand and metal ion and is consistent with variations seen with inorganics[9,43] and organics.[9,35,36]

For Co(CN)$_6^{3-}$ the lowest excited state is a triplet, and emission studies suggest $E_t \sim$ 15-22 kK.[44] Biacetyl with E_t $\sim$ 20 kK sensitizes the aquation of Co(CN)$_6^{3-}$.[45,46] With both Ru(bipy)$_3^{2+}$ and Ru(phen)$_3^{2+}$ $k_2{}^0$ is $\sim$1000 smaller than the diffusional limit and equally small relative to the K_{sv}'s for compounds having similar electronic energy level patterns and ligands (Ni(CN)$_4^{2-}$ and Cr(CN)$_6^{4-}$). Therefore, the E_0's for both donors lie below the Co(CN)$_6^{3-}$ triplet state. Consequently, for Co(CN)$_6^{3-}$ in solution, $\sim$18.4 kK $< E_t < \sim$20 kK. Hipps and Crosby[47] carried out a detailed analysis of the low temperature emission spectra and estimated $E_t \geq 17.1$ kK which is consistent with our value. Further work with other transition metal donors will permit more accurate estimates of these solution E_t's as well as others.

Acknowledgment is made to the NIH for a Biomedical Science Support Grant administered by the University of Virginia, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation for a Cottrell Research Grant, to the National Science Foundation, and to the Department of Chemistry. We thank A. W. Norvelle, Jr., and S. Marrs for their assistance in constructing the spectrofluorimeter and decay time apparatus and V. Balzani for preprints.

References and Notes

(1) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **93**, 1800 (1971).

(2) P. Natarajan and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 3635 (1972).

(3) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc.*, **95**, 5159 (1973).

(4) M. Wrighton and J. Markham, *J. Phys. Chem.*, **77**, 3042 (1973).

(5) (a) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974); (b) C. R. Bock, T. J. Meyer, and D. G. Whitten, *ibid.*, **97**, 2909 (1975); (c) A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *ibid.*, **98**, 1047 (1976); (d) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976).

(6) G. S. Laurence and V. Balzani, *Inorg. Chem.*, **13**, 2976 (1974).

(7) (a) H. Gafney and A. W. Adamson, *J. Am. Chem. Soc.*, **94**, 8238 (1972); (b) G. Navon and N. Sutin, *Inorg. Chem.*, **13**, 2159 (1974); (c) H. Gafney and A. W. Adamson, submitted.

(8) C. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976).

(9) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).

(10) N. Sabbatini, M. A. Scandola, and V. Balzani, *J. Phys. Chem.*, **78**, 541 (1974).

(11) I. Fujita and H. Kobayashi, *J. Chem. Phys.*, **59**, 2902 (1973).

(12) J. N. Demas, D. Diemente, and E. W. Harris, *J. Am. Chem. Soc.*, **95**, 6864 (1973).

(13) J. N. Demas, E. W. Harris, C. M. Flynn, Jr., and D. Diemente, *J. Am. Chem. Soc.*, **97**, 3838 (1975).

(14) (a) J. N. Demas, E. W. Harris, and R. P. McBride, "Lasers in Physical Chemistry and Biophysics", J. Joussot-Dubien, Ed., Elsevier, 1975, p 477; (b) J. N. Demas, R. P. McBride, and E. W. Harris, *J. Phys. Chem.*, in press.

(15) J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **96**, 3663 (1974).

(16) F. Bolleta, M. Maestri, L. Moggi, and L. Balzani, *J. Phys. Chem.*, **78**, 1374 (1974).

(17) F. Scandola, O. Traverso, and V. Carassiti, *Mol. Photochem.*, 1, 11 (1969).

(18) S. Y. Tyree, Jr., Ed., *Inorg. Synth.*, **9**, 160 (1967).

(19) W. C. Fernelius, Ed., *Inorg. Synth.*, **2**, 227 (1946).

(20) J. N. Demas, M. Weiss, and D. Diemente, work in progress.

(21) J. N. Demas and C. M. Flynn, Jr., *Anal. Chem.*, **48**, 353 (1976).

(22) A. Weller, *Prog. React. Kinet.* **1**, 187 (1961).

(23) J. N. Demas, *J. Chem. Educ.*, in press.

(24) S. Glasstone, "Textbook of Physical Chemistry", 2d ed, Van Nostrand, New York, N.Y., 1946.

(25) (a) F. Bolleta, M. Maestri, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **95**, 7866 (1973); (b) F. Bolletta, M. Maestri, and F. Moggi, *J. Phys. Chem.*, **77**, 861 (1973).

(26) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

(27) P. D. Fleischauer, A. W. Adamson, and G. Sartori, "Inorganic Reaction Mechanisms Part II", J. O. Edwards, Ed., Wiley, New York, N.Y., 1972, p 1.

(28) R. W. Harrigan, G. D. Hager, and G. A. Crosby, *Chem. Phys. Lett.*, **21**, 487 (1973).

(29) G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., *J. Am. Chem. Soc.*, **96**, 629 (1974).

(30) J. N. Demas, J. W. Addington, and S. Peterson, submitted.

(31) M. T. Beck, *Coord. Chem. Rev.*, **3**, 91 (1968).

(32) I. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem.*, **76**, 115 (1972).

(33) P. J. Wagner and I. Kochevar, *J. Am. Chem. Soc.*, **90**, 2232 (1968).

(34) K. H. Grellmann, A. R. Walkins, and A. Weller, *J. Phys. Chem.*, **76**, 3123 (1972).

(35) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969.

(36) H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, **82**, 2411 (1960).

(37) R. Ballardini, G. Varani, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **96**, 7123 (1974).

(38) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970).

(39) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

(40) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961).

(41) D. W. H. Carstens, private communications.

(42) P. C. Ford, J. D. Peterson, and R. E. Hintze, *Coord. Chem. Rev.*, **14**, 67 (1974).

(43) A. Pfeil, *J. Am. Chem. Soc.*, **93**, 5395 (1971).

(44) G. A. Crosby, *J. Chim. Phys. Phys.-Chim. Biol.*, **64**, 160 (1967).

(45) G. B. Porter, *J. Am. Chem. Soc.*, **91**, 3981 (1969).

(46) M. A. Scandola and F. Scandola, *J. Am. Chem. Soc.*, **94**, 1805 (1972).

(47) K. W. Hipps and G. A. Crosby, *Inorg Chem.*, **13**, 1543 (1974); *J. Phys. Chem.*, in press.