= H. Similarly, when a THF solution of pure 3,6-diphenyl-3,6-dihydropyrazine (**5**, R = H) was stirred with $Mo(CO)_6$ in THF for 3 days, **5** R = H, was recovered unchanged. Clearly, the pyrazine **3** is formed from **4** but not **5**, perhaps because it would be sterically more difficult for the metal carbonyl groups to abstract the allylic hydrogens in **13** than in **11**. The formation of **13**, if any occurs, would thus be reversible. The failure to observe any 2,3-diarylpyrazines, or their dihydro derivatives, in any of these reactions may be due to steric effects in coupling of the two organic ligands in **9**.

An investigation of the reactions of azirines, and related systems, with other metal carbonyls is currently in progress.

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Steady-State Considerations in the Electron-Transfer Quenching of the Tris(2,2′-bipyridine)ruthenium(II) Luminescence

Sir:

Recent studies have shown that electron transfer provides an efficient mechanism for the quenching of tris(2,2′-bipyridine)ruthenium(II) luminescence by certain metal complexes and organic molecules.[1-4] Direct evidence for an electron-transfer quenching mechanism is provided by the detection of $Ru(bipy)_3{}^{3+}$ and the reduced quencher both in flash experiments on reversible systems[2] and after the continuous irradiation of irreversible systems.[1,3,4] Indirect evidence for electron-transfer rather than energy-transfer quenching mechanisms can also be obtained in suitable systems from relative rate and spectroscopic considerations.[3] Another approach that might be used to distinguish between these mechanisms is the measurement of the degree of oxidation (or reduction) of the sensitizer under steady-state conditions. To the best of our knowledge this method has not been used previously, and in this paper we report a measurement of the steady-state concentrations of $Ru(bipy)_3{}^{3+}$ and Fe^{2+} produced in the irradiation of $Ru(bipy)_3{}^{2+}$ in the presence of Fe^{3+} ions. The back electron-transfer reaction between $Ru(bipy)_3{}^{3+}$ and Fe^{2+} is sufficiently slow that the concentration of these products attains appreciable steady-state values (Scheme I). In this scheme $Ru(bipy)_3{}^{3+}|Fe^{2+}$ and $Ru(bipy)_3{}^{2+}|Fe^{3+}$ represent the ground-state precursor and successor complexes, respectively, and energy transfer quenching (k_{en}) leading to $Ru(bipy)_3{}^{2+}|{}^*Fe^{3+}$ is not shown.[5] In terms of this scheme[7] the steady-state concentrations [X] of $Ru(bipy)_3{}^{3+}$ or Fe^{2+} ions in a sample of given $Ru(bipy)_3{}^{2+}$(D) and Fe^{3+}(Q) concentrations is given by

Scheme I

$$\begin{tikzcd}
{}^*\mathrm{Ru(bipy)_3}^{2+} + \mathrm{Fe}^{3+} \arrow[r, "k_{el}"] \arrow[d, shift left, "k_0"] & \mathrm{Ru(bipy)_3}^{3+} \mid \mathrm{Fe}^{2+} \arrow[r, shift left, "k_2"] \arrow[d, "k_1"] & \mathrm{Ru(bipy)_3}^{3+} + \mathrm{Fe}^{2+} \arrow[l, shift left, "k_{-2}"] \\
\mathrm{Ru(bipy)_3}^{2+} + \mathrm{Fe}^{3+} \arrow[u, shift left, "h\nu"] \arrow[r, shift left] & \mathrm{Ru(bipy)_3}^{2+} \mid \mathrm{Fe}^{3+} \arrow[l, shift left] &
\end{tikzcd} \tag{1}$$

$$k_{el}[{}^*D][Q] = \frac{k_1 k_{-2}[X]^2}{k_2} \tag{2a}$$

If the absorbance of the quencher at the excitation wavelength may be neglected and the absorbance of the donor is not too large, then the expression for the concentration of the excited donor in a 1-cm path length cell can be simplified from eq 8 of a previous paper[3] to give

$$[{}^*D] = \frac{2.3 \times 10^3 I^{in} A_D}{k_0 + k_q[Q]} \tag{2b}$$

where $A_D = \epsilon_D([D_0] - [X])$, A_D and ϵ_D are the absorbance of $Ru(bipy)_3{}^{2+}$ (corrected for $Ru(bipy)_3{}^{3+}$ concentration) and its molar absorptivity, respectively, $[D_0]$ is the total ruthenium concentration in the presence of the quencher, $k_q = (k_{en} + k_{el})$, I^{in} is the incident light intensity, and the concentrations of the precursor and successor complexes have been neglected. Since the emission intensity (I^{em}) is proportional to [*D], the ratio of measured emission intensities (at constant incident light intensity) from a sample containing Q to that from a reference sample without Q is

$$\frac{I^{em}}{I_{ref}{}^{em}} = \frac{[{}^*D]}{[{}^*D]_{ref}} = \frac{\{[D_0] - [X]\}k_0}{[D]_{ref}\{k_0 + k_q[Q]\}} \tag{2c}$$

Equations 2a and 2b can be combined to yield eq 3a which is an expression for the steady-state concentrations in

$$\left\{\frac{[X_1]}{[X_2]}\right\}^2 = \frac{I_1{}^{in}\{[D_0] - [X_1]\}}{I_2{}^{in}\{[D_0] - [X_2]\}} \tag{3a}$$

a given sample at two different light intensities. Similarly, eq 3b is an expression for the emission intensities of a given

$$\frac{[D_0] - [X_1]}{[D_0] - [X_2]} = \left[\frac{I^{em}}{I_{ref}{}^{em}}\right]_1 \left[\frac{I^{em}}{I_{ref}{}^{em}}\right]_2^{-1} \tag{3b}$$

sample relative to that of an unquenched reference sample at the two light intensities. Values of [X] as a function of light intensity can now be obtained by the simultaneous solution of eq 3a and 3b.

Emission intensity measurements were made on a Perkin-Elmer model MPF-4 fluorescence spectrophotometer equipped with a 150-W Xenon lamp. Incident light intensities were determined using ferrioxalate actinometry[8] and were successively reduced with neutral density filters. An

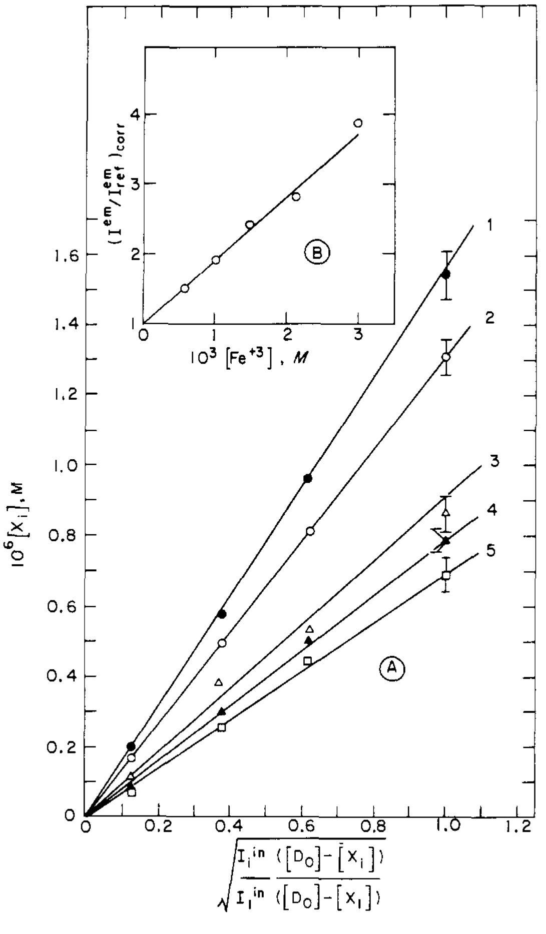

Figure 1. (A) Plot of the steady-state concentration in deaerated solutions vs. the square root of corrected incident light intensity ratios with $I_1^{in} = 1.12 \times 10^{-8}$ einstein cm^{-2} sec^{-1} at 25° and 0.11 M ionic strength adjusted with $HClO_4$: 1, $[Ru(bipy)_3{}^{2+}] = 6.15 \times 10^{-6}$ M, $[Fe^{3+}] = 3.00 \times 10^{-3}$ M; 2, $[Ru(bipy)_3{}^{2+}] = 4.92 \times 10^{-6}$ M, $[Fe^{3+}] = 2.10 \times 10^{-3}$ M; 3, $[Ru(bipy)_3{}^{2+}] = 3.69 \times 10^{-6}$ M, $[Fe^{3+}] = 1.50 \times 10^{-3}$ M; 4, $[Ru(bipy)_3{}^{2+}] = 3.07 \times 10^{-6}$ M, $[Fe^{3+}] = 1.05 \times 10^{-3}$ M; 5, $[Ru(bipy)_3{}^{2+}] = 2.46 \times 10^{-6}$ M, $[Fe^{3+}] = 0.60 \times 10^{-3}$ M. (B) The corrected Stern–Volmer plot for quenching of $*Ru(bipy)_3{}^{2+}$ emission by Fe^{3+} at 25° and 0.11 M ionic strength adjusted with $HClO_4$.

excitation wavelength of 452 nm was used and the emission was monitored at 608 nm. The corrections for iron(III) absorbance were negligible at these wavelengths. To enhance the sensitivity of the measurements, the ratio of emission intensities ($I^{em}/I_{ref}{}^{em}$) at the unfiltered incident light intensity (1.12×10^{-8} einstein cm^{-2} sec^{-1}) was adjusted to about unity by using a relatively dilute reference solution ($[Ru(bipy)_3{}^{2+}] = 1.23 \times 10^{-6}$ M in 0.11 M $HClO_4$). All of the measurements were made at an ionic strength of 0.11 M (adjusted with perchloric acid) or in 0.50 M perchloric acid at 25°.

The steady-state concentrations (calculated from eq 3a and 3b) are plotted vs. the square roots of incident light intensity ratios in Figure 1 which also contains the usual Stern–Volmer plot corrected for the loss of emission intensity resulting from the formation of $Ru(bipy)_3{}^{3+}$. It will be seen that the measurements satisfy eq 3 reasonably well and that the steady-state concentration of $Ru(bipy)_3{}^{3+}$ is about 25% of the initial $Ru(bipy)_3{}^{2+}$ concentration at the highest light intensity used. The Stern–Volmer constants for quenching by Fe^{3+} determined in this work are 9.0×10^2 and 1.4×10^3 M^{-1} at 0.11 and 0.50 M ionic strength, respectively.

Three more experiments were performed to confirm that the primary quenching products are $Ru(bipy)_3{}^{3+}$ and Fe^{2+}. By adding excess Fe^{2+} (1.5×10^{-4} M) to the reaction system, the $Ru(bipy)_3{}^{3+}$ concentrations in the steady state were so reduced that the emission intensity ratios from a given sample were no longer dependent on the incident light intensity. Secondly, using $Ru(NH_3)_6{}^{3+}$, a quencher for which the back-electron-transfer rate approaches the diffusion-controlled limit, no variation of emission intensity ratios as a function of incident light intensity was observed. Finally, for quenching of $*Os(bipy)_3{}^{2+}$ emission by $Co(phen)_3{}^{3+}$, the emission intensity ratios were independent of the incident light intensity. For this system, the short lifetime of the $*Os(bipy)_3{}^{2+}$ ion[9] coupled with an order of magnitude faster back-electron-transfer reaction[10] considerably reduces the steady-state concentrations.

The quenching of $*Ru(bipy)_3{}^{2+}$ emission by Fe^{3+} has recently been investigated by Laurence and Balzani.[4] The quenching rate constant ($k_q = k_{en} + k_{el}$) of 1.9×10^9 M^{-1} sec^{-1} in 0.5 M $HClO_4$ at 20° determined in that work is in good agreement with the values of 1.5×10^9 and 2.3×10^9 M^{-1} sec^{-1} at 0.11 and 0.50 M ionic strength, respectively, obtained in this study. Much higher reference $Ru(bipy)_3{}^{2+}$ concentrations (~5×10^{-5} M) were employed in the earlier study, and as a consequence the steady-state concentration of $Ru(bipy)_3{}^{3+}$ was relatively unimportant.

The back-electron-transfer reaction between $Ru(bipy)_3{}^{3+}$ and Fe^{2+} has been observed previously[2] and confirmed by us using a laser flash photolysis technique. The rate constant for this reaction has also been measured by flow techniques and is 7.2×10^5 M^{-1} sec^{-1} in 0.5 M $HClO_4$ and $(6.41 \pm 0.38) \times 10^5$ M^{-1} sec^{-1} in 1.0 M $HClO_4$ at 25°.[11,12] Since this rate constant is equal to $k_{-2}k_1/k_2$, the value of k_{el} can be calculated from $k_{el}k_2/k_{-2}k_1 = (2.5 \pm 0.4) \times 10^3$ and $(2.6 \pm 0.3) \times 10^3$ at 0.11 and 0.5 M ionic strength, respectively, determined in this work. This calculation gives $k_{el} = (1.9 \pm 0.3) \times 10^9$ M^{-1} sec^{-1} at 0.5 M ionic strength, corresponding to about 81 ± 16% of electron-transfer quenching.[13,14]

The successful application of this type of steady-state measurement depends upon two factors, a high value of the rate constant for electron-transfer quenching, and a high value of the ratio of the rate constants for the dissociation of the precursor complex (cage escape) to electron transfer within the complex (cage). Both of these conditions are satisfied in the $Ru(bipy)_3{}^{2+/3+}$-$Fe^{3+/2+}$ system. The emission intensity measurements indicate that the electron-transfer quenching of $*Ru(bipy)_3{}^{2+}$ by Fe^{3+} is close to diffusion controlled, and the rate constant for the oxidation of Fe^{2+} by $Ru(bipy)_3{}^{3+}$ indicates that $k_2 \gg k_1$, assuming k_{-2} to be diffusion controlled. Evidently electron transfer within the complex (cage) which is determined by k_1, is about 10^3 times slower than the dissociation of the complex (cage escape) which is determined by k_2. Further experiments are in progress to ascertain the factors favoring cage escape over cage recombination and to elucidate the detailed mechanisms of the quenching reactions. Finally, in view of the relatively high steady state concentration of the electron transfer products built up under illumination, systems of this type could find important application in photogalvanic cells.[15]

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been estimated to lie about 12.3 kK or 1.5 V above the $^6A_{1g}$ ground state.[6] This excited state could be a powerful oxidant and might accept an electron from $Ru(bipy)_3^{2+}$ in the primary cage to form $Ru(bipy)_3^{3+}$ and Fe^{2+}. These products would, of course, be indistinguishable from those formed by direct electron transfer quenching.

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(15) We have measured potentials of ~100 mV in a photogalvanic cell utilizing the reversible $Ru(bipy)_3^{2+}$-Fe^{3+} system.

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Solid State Structure and Oxidation States in Bis(diphenylglyoximato)nickel and -palladium Iodides

Sir:

Partial oxidation of stacked, square-planar, d^8 transition metal complexes may represent an effective method of increasing the metal-metal interaction and anisotropic electron transport in one-dimensional solid state "chain" compounds.[1] The Krogmann salt, $K_2Pt(CN)_4Br_{0.30}\cdot 3\ H_2O$, is the most thoroughly studied prototype to date.[1,2] The complexes $M(dpg)_2I$, dpg = diphenylglyoximate ($(C_6H_5)_2$-$C_2N_2O_2H^-$) and M = Ni, Pd,[3] which have moderately high electrical conductivity,[4] are potentially new examples of such compounds. Based principally upon indirect chemical evidence and limited photographic X-ray data, the form of the iodine has been assigned both as I_2 (metal unoxidized, i.e., a halogen charge-transfer complex[5]) and as I_3^- (metal partially oxidized, i.e., a triiodide chain compound[6]);[7] a priori, I^- is also conceivable.[8] Though the basic one-dimensional character of this material had been suggested,[7a] we thought it important to investigate the nature of the structure and oxidation states in greater detail. We report here structural and spectroscopic studies which unambiguously establish the structure and indicate that the nickel and palladium atoms have formal fractional oxidation states as in the Krogmann compound.

Crystals of $Ni(dpg)_2I$ suitable for diffraction were grown by very slow cooling of *o*-dichlorobenzene solutions containing an excess of iodine. The compound crystallizes in the tetragonal space group D_{4h}^8-$P4/ncc$ with four formula units of $Ni(dpg)_2I$ in a cell of dimensions a = 19.887 (4) and c = 6.542 (2) Å.[9] Intensity data were collected on a diffractometer using Mo $K\alpha$ radiation. The structure was solved by direct methods and was refined by full-matrix, least-squares techniques to an R index on F_o of 0.092 for the 31 variables and 294 observations above background. A listing of positional and thermal parameters will appear in the microfilm edition; see paragraph at end of paper regarding supplementary material. A view of the structure down the c axis is shown in Figure 1. The $Ni(dpg)_2$ units stack (staggered by 90°) at intervals of 3.271 (1) Å. The Ni-Ni distance is thus ca. 0.28 Å shorter than that of unoxidized $Ni(dpg)_2$ (3.547 Å),[10] but longer than that of $Ni(dmg)_2$ (3.25 Å)[11] and nickel metal (2.49 Å).[12] The crystallographically imposed coordination geometry about the Ni atom is distorted from planar D_{2h} (as in $Ni(dmg)_2$[11]) to D_2 symmetry, with coordinated N atoms displaced 0.16 (1) Å above or below the mean molecular plane. The Ni-N (1.86 (2) Å), N-C (1.30 (3) Å), N-O (1.34 (3) Å), and O-O (2.43 (4) Å) distances are not significantly different from those of $Ni(dmg)_2$.[11] The iodine atoms are found in chains, filling "tunnels" defined by the phenyl rings. The closest C(phenyl)-I (4.13 (3) Å) and H(phenyl)-I (3.40 (1) Å) contacts indicate only van der Waals' phenyl-iodine interaction. The Ni/I ratio in this compound is 1.012 ± 0.020, as determined from the refinement of the occupancy of the I atom. The I positions are equally spaced at one half the c axis length (3.271 (1) Å). The root-mean-square amplitudes of vibration of the iodine perpendicular to the chain are normal at 0.234 (4) Å but abnormally large parallel to the chain at 0.756 (11) Å. The large amplitude along the chain is a manifestation of disorder, the nature of which cannot be resolved from the X-ray data as a number of different models lead to the same electron density distribution. In particular, the presence of discrete I-I units (separation 2.72-2.75 Å)[13] or discrete I-I-I^- units (I-I separation ca.

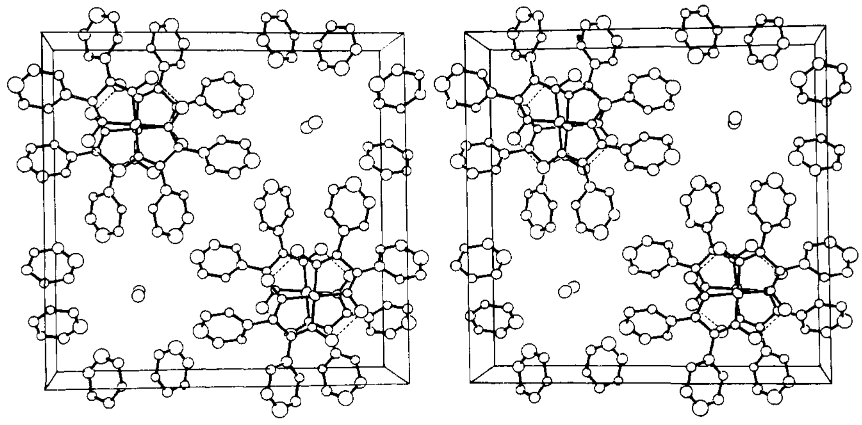

Figure 1. Stereoscopic view down the c axis of the unit cell of $Ni(dpg)_2I$, showing the channels surrounding the iodine chains. Dotted lines indicate the diphenylglyoximate O-H-O bonds. For all atoms, 50% probability thermal ellipsoids are shown; Ni and I were refined anisotropically.