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Excited-State Coordination Chemistry: A New Quenching Mechanism

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The quenching of Ru(II) diimines has provided unique insights into the excited-state chemistry of transition-metal complexes. Quenching by inorganic and organic reagents, molecular oxygen, and hydrogen ion has elucidated an excited-state redox chemistry, inter- and intramolecular energy transfer processes, and striking excited-state acid−base properties.[1−11] Here, we present evidence for another type of quenching mechanism which results in an excited-state coordination chemistry and leads to an unusual photochemical reaction that ***increases*** the metal content of the complex. In this case, optical excitation of $Ru(bpy)_2(dpp)^{2+}$ (bpy = bipyridyl; dpp = 2,3-dipyridylpyrazine) produces an metal-to-ligand charge transfer (MLCT) state localized on the dpp ligand.[12] The increased electron density in the excited state increases the basicity of the dpp ligand's peripheral nitrogens,[11] and this increase in basicity leads to coordination to a second metal ion.

$Ru(bpy)_2(dpp)^{2+}$ has been widely used to assemble polymetallic complexes.[12−16] Refluxing the complex in the presence of a variety of transition metal salts and complexes results in coordination at the peripheral nitrogens and, depending on the number of dpp ligands attached to Ru(II), formation of polymetallic complexes. Refluxing $Ru(bpy)_2(dpp)^{2+}$ and $PtCl_6^{2-}$ in ethanol, for example, changes the solution color from reddish-orange to purple, and chromatographic separation of the reaction mixture confirms $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formation. The color change is due to coordination of Pt(IV) at the dpp peripheral nitrogens which shifts the MLCT transition to dpp from 470 nm in $Ru(bpy)_2(dpp)^{2+}$ to 525 nm in $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$. In water at 30 °C and μ = 1.0 M (NaCl), the rate law for the thermal reaction is $R = k_{th}[Ru(bpy)_2(dpp)^{2+}][PtCl_6^{2-}]$ where $k_{th} = 1.8 \pm 0.4 \times 10^{-4}$ M^{-1} s^{-1} and, in the 30 to 50 °C range, $E_a = 15 \pm 2$ kcal/mol.

Spectra recorded periodically during a 457-nm photolysis of an aqueous solution 10^{-4} M in $Ru(bpy)_2(dpp)^{2+}$ and 10^{-2} M in $PtCl_6^{2-}$ (Figure 1) show a decline in absorbance at 470 nm and a corresponding increase at 525 nm. The spectral changes, which occur in a matter of minutes, are identical to those recorded during the thermal reaction, and thin-layer chromatography of the photolyte and isolation of the photoproduct confirm $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formation. Isosbestic points at 398 and 483 nm (Figure 1) indicate a quantitative conversion through ≥60−70% reaction. Similar spectral changes indicative of dimer formation occur with $OsCl_6^{2-}$, $RhCl_6^{3-}$, and $PdCl_6^{2-}$, although with the latter complex, the extent of the quantitative conversion is limited by the hydrolysis of the hexachloride.

At μ = 3.0 M (NaCl), the Stern−Volmer constants from intensity and lifetime quenching of the 675-nm emission of $Ru(bpy)_2(dpp)^{2+}$ by $PtCl_6^{2-}$, 403 ± 35 M and 397 ± 43 M, respectively, are within experimental error (Figure 2) and in excellent agreement with the Stern−Volmer constant, 413 ± 62 M, obtained from the ratio of the slope to intercept of plots of the reciprocal of the quantum efficiency of $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formation, Φ_{bi}, versus the reciprocal of the concentration of $PtCl_6^{2-}$ (Figure 3). The equivalence of the values obtained from the different techniques establishes that, at high ionic strength, formation of $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ occurs via a diffusional encounter between the excited $Ru(bpy)_2(dpp)^{2+}$ and $PtCl_6^{2-}$. The intercept in Figure 3 yields a limiting value of $\Phi_{bi} = 0.18 \pm 0.02$, and taking 135 ± 14 ns as the lifetime of the MLCT state of $Ru(bpy)_2(dpp)^{2+}$,[12] the relation $K_{sv} = k_b\tau$ yields $2.84 \pm 0.56 \times 10^9$ M^{-1} s^{-1} for the bimolecular rate constant. Bimetallic formation occurs with higher efficiency at low ionic strength, but the reaction occurs via optical excitation of $[Ru(bpy)_2(dpp)^{2+}, PtCl_6^{2-}]$ ion pairs.

Bimetallic formation is an unusual photochemical reaction that does not occur with metals known to quench by electron- or energy-transfer processes. Fe^{3+} and Cr^{3+} quench by electron and energy transfer, respectively, and form stable diimine complexes. Cr^{3+} is also substitution inert, yet neither ion reacts with $^*Ru(bpy)_2(dpp)^{2+}$ to form a bimetallic, $\Phi_{bi} \leq 10^{-3}$. Bimetallic formation is also energetically inconsistent with either photoinduced electron or energy transfer. The emission from $Ru(bpy)_2(dpp)^{2+}$ places the MLCT state localized on dpp 1.48 eV above the ground state, while the absorption spectrum of $PtCl_6^{2-}$ indicates that the $^1T_1$ state lies 3.5 eV above the ground state. Lower energy, weaker absorptions of $PtCl_6^{2-}$ place the spin forbidden $^3T_2$ state at 2.8 eV, and from the Tanabe−Sugano diagram, the $^3T_1$ state is calculated to lie at 2 eV above the ground state.[17] Clearly, uncertainties exist in the latter, yet neither state is expected to be <1.48 eV, making energy transfer endergonic. The reaction is also not due to a trivial photolysis of the hexachlorides followed by coordination to $Ru(bpy)_2(dpp)^{2+}$. Although the quantum efficiency of $PtCl_6^{2-}$ decomposition with 488-nm excitation is 0.32 ± 0.02, under the conditions of the above experiments where ≥90% of the excitation is absorbed by $Ru(bpy)_2(dpp)^{2+}$, direct photolysis of $PtCl_6^{2-}$ at best accounts for

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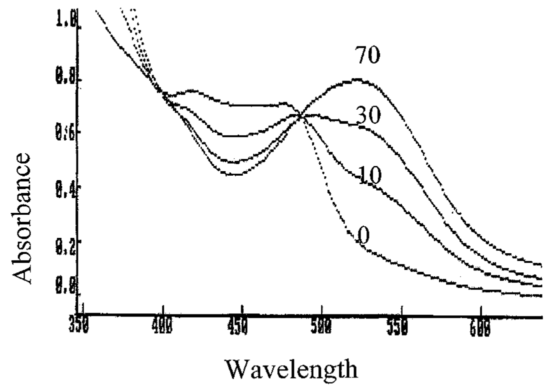

Figure 1. Spectral changes during a 450-nm photolysis of a 10^{-4} M $Ru(bpy)_2(dpp)^{2+}$ and 10^{-3} M $PtCl_6^{2-}$ solution. Numbers refer to irradiation times in seconds.

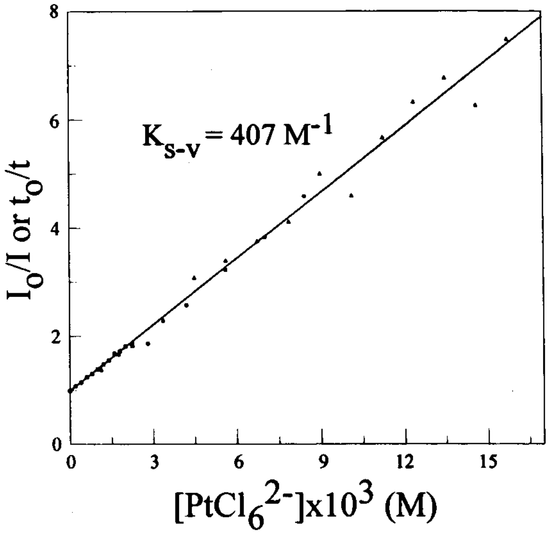

Figure 2. Intensity (■) and lifetime (▲) quenching of the 675-nm emission of $Ru(bpy)_2(dpp)^{2+}$ by $PtCl_6^{2-}$, $\mu = 3.0$ M (NaCl).

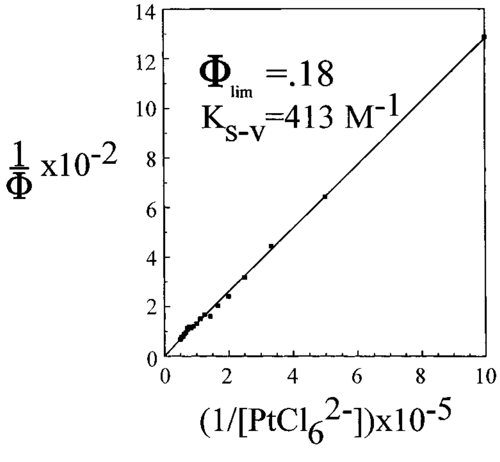

Figure 3. Reciprocal of the quantum yield of $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formation as a function of the reciprocal of the $PtCl_6^{2-}$ concentration, $\mu = 3.0$ M (NaCl).

≤20% of the $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formed.[18] Competitive quenching by Fe(III), $K_{sv} = 650 \pm 78$ M^{-1}, eliminates bimetallic formation, $\Phi_{bi} \leq 10^{-5}$, further establishing that formation of the bimetallic occurs via excitation $Ru(bpy)_2(dpp)^{2+}$, rather than excitation of the hexachloride to form a coordinatively unsaturated intermediate which then reacts with $Ru(bpy)_2(dpp)^{2+}$.

Photoinduced electron transfer is also energetically unlikely. The emission maximum of $Ru(bpy)_2(dpp)^{2+}$, 675 nm, and the reversible oxidation potential of the ground state, 1.54 eV (vs NHE), yield 0.29 eV as the MLCT state oxidation potential. The one-electron reduction potential of $PtCl_6^{2-}$ is not available, but assuming that entropy factors are negligible, the $\Delta H°_f$ of $PtCl_{3(s)}$ suggests that oxidative quenching is endergonic by as much as 4 eV.[19] Reductive quenching seems equally unlikely since it would

$$*Ru(bpy)_2(dpp)^{2+} + PtCl_6^{2-} \rightarrow Ru(bpy)_2(dpp)^{3+} + Pt(III) \tag{1}$$

yield the unlikely oxidation state Pt^{5+}. Similar estimates of the reduction potentials of $OsCl_6^{2-}$, $RhCl_6^{3-}$, and $PdCl_6^{2-}$ suggest that one-electron reductions are also endergonic.[18] Furthermore, bimetallic formation does not occur, $\Phi_{bi} \leq 10^{-3}$, with Fe^{3+} even though electron-transfer quenching is exergonic by 1.0 eV, and yields Fe^{2+} which readily coordinates with diimines. Nevertheless, mechanistic distinctions based on energies and calculated efficiencies are fraught with uncertainties, but central to each is the formation of a more labile intermediate. In aqueous solution, formation of a labile oxidation state or a coordinatively unsaturated intermediate would result in water coordination, ligand scrambling, and a distribution of products containing differing amount of coordinated water. With $PtCl_6^{2-}$, $OsCl_6^{2-}$, and $RhCl_6^{3-}$, however, formation of the bimetallic is quantitative as evidenced by the maintenance of two isosbestic points through as much as 70% conversion to the bimetallic, at which point photolysis of the bimetallic occurs.

The emissive MLCT state in $Ru(bpy)_2(dpp)^{2+}$ is localized on dpp, and the increase in electron density in the π^* orbital increases the basicity of the peripheral nitrogens of dpp by $\geq 10^3$ relative to the ground state.[11] We propose that the increased electron density corresponding to this immense increase in basicity, rather than energy or electron transfer, leads to coordination of the second metal ion. Since the increased electron density exists only in the excited state, coordination to the second metal is viewed as exiplex formation. Formation of the thermodynamically stable bimetallic is attributed to the chelate effect, i.e., the second peripheral nitrogen on dpp binds competitively with relaxation of the bimetallic exiplex. With a monodentate ligand, optical excitation will increase basicity, but quenching may not result in a net chemistry since dissociation will occur on relaxation to the ground state. In the above examples, optical excitation increases electron density as evidenced by the increase in basicity, and the increased electron density leads to coordination. In other Ru(II) diimines, however, optical excitation reduces basicity[3] and may result in a dissociative excited state that recombines upon relaxation to the ground state.[20] As with photoredox chemistry, complementary thermal back reactions, particularly in the latter case, offer the potential of using time-resolved photochemical techniques to examine ligand substitution reactions.

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(18) Definitive information on the nature of the $PtCl_6^{2-}$ primary photoproduct, and its lifetime in aqueous solution is not currently available. Nevertheless, in calculating the fraction of reaction that could occur via direct photolysis of $PtCl_6^{2-}$, we assume that direct photolysis leads to a coordinatively unsaturated primary photoproduct and that this species is sufficiently long-lived to react with $Ru(bpy)_2(dpp)^{2+}$ with unitary efficiency.

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