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Coordination Chemistry Reviews
171 (1998) 71–84

Excited state acid–base chemistry
A new quenching mechanism

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Received 7 July 1997; received in revised form 25 September 1997; accepted 19 November 1997

Contents

Abstract

Most photochemical reactions degrade a metal complex, but recent experiments in this laboratory reveal a series of unusual photochemical reactions that increase the metal content of the complex. A 450 nm excitation of bis(2,2′-bipyridine)(2,3-bis(2-pyridyl) pyrazine)ruthenium(II), Ru(bpy)$_2$dpp^{2+}, complexes in the presence of PtCl$_6^{2-}$, PdCl$_6^{2-}$ and RhCl$_6^{3-}$ results in quantitative formation of the corresponding bimetallic [Ru(bpy)$_2$(dpp)MCl$_4$]$^{2+}$. The excited state energies and thermal redox potentials of the chlorides and the specificity of the reaction suggest that formation of the bimetallic is not the consequence of energy transfer or electron transfer quenching. Instead, we propose that these reactions are the result of an excited state acid–base chemistry that manifests itself as changes in coordination and nucleophilicity. The emissive MLCT state in Ru(bpy)$_2$(dpp)$^{2+}$ is localized on dpp, and H$^+$ quenching indicates that population of the emissive MLCT state increases the basicity of at least one of the peripheral nitrogens by at least four orders of magnitude relative to that in the ground state. Population of the MLCT state (bpy)$_2$Ru(CN)$_2$, on the other hand, shifts charge density to the bpy ligand thereby decreasing the basicity of the

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PII S0010-8545(98)00027-7

cyanide ligand by ca. four orders of magnitude. The pH dependence of the quantum yield of decomposition of *trans*-$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ suggests that this immense change in basicity leads to a dissociative excited state. In complexes that exhibit excited state acid–base properties, the data presented here suggest that quenching is not necessarily limited to electron or energy transfer, but also occurs by an excited state acid–base chemistry that leads to changes in coordination and/or nucleophilicity.

Keywords: Excited state; Quenching mechanism

1. Introduction

Although the energy crisis of the mid-seventies focused attention on the newly discovered excited state redox properties of Ru(II) diimines [1], studies of the quenching of the MLCT state of these complexes by organic and inorganic reagents have elucidated a variety of bimolecular processes [2,3]. The chemistry arising from these processes is similar to that occurring in the ground state, but distinguished by the energy of the reactive excited state. Unlike a thermal redox reagent, for example, the difference between the emission energy and the energy of the reversible, one-electron oxidation and reduction potentials (vs. NHE) shows that the luminescent MLCT state of $Ru(bpy)_3^{2+}$, designated $^*Ru(bpy)_3^{2+}$, is energetically capable of acting as either an oxidant or reductant:

$$^*Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e^- \quad E = 0.88\ \text{eV} \tag{1}$$

$$^*Ru(bpy)_3^{2+} + e^- \rightarrow Ru(bpy)_3^{+} \quad E = 0.71\ \text{eV} \tag{2}$$

The intent is not to imply that all excited state redox reagents are equally strong oxidants and reductants. Excited state redox potentials can be systematically varied by means of different ligands and ligand substituents [2,3]. Rather, $Ru(bpy)_3^{2+}$ emphasizes the important difference imparted by the energy of the reactive MLCT state. A thermal redox reaction yields thermodynamically stable products, whereas an excited state electron transfer yields products that are stable relative to the excited state, but unstable relative to the ground state of the precursor. The result is transient products and, unless the experiments are specifically designed to detect the redox products, the impression is that no chemical change has occurred. To illustrate the point, oxidative quenching of $^*Ru(bpy)_3^{2+}$ by a quencher Q:

$$^*Ru(bpy)_3^{2+} + Q \xrightarrow{k_e} Ru(bpy)_3^{3+} + Q^- \tag{3}$$

yields Q^- and the powerful oxidant $Ru(bpy)_3^{3+}$. Unless one or more of the electron transfer products undergoes a subsequent reaction or change [1–3], the complementary thermal back reaction

$$Ru(bpy)_3^{3+} + Q^- \xrightarrow{k_{th}} Ru(bpy)_3^{2+} + Q \tag{4}$$

occurs and the redox products are transitory [4].

Reversibility is a challenge with respect to charge separation, but a benefit in kinetics. Considered to be outer-sphere electron-transfer reagents, the substitution inert 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) complexes of the low-spin iron triad have proven to be very useful in testing different aspects of Marcus–Hush theory. The large oxidation potentials of the trivalent metal complexes, however, favor reaction rates that are often too rapid for conventional techniques. The ability to "turn the complex on" and generate non-equilibrium redox products within the time resolution of current pulsed laser technology allows flash photolysis to be used as a relaxation technique to probe thermal redox chemistry in previously unaccessible time domains [5].

Energy transfer quenching of the MLCT states of Ru(II) diimines has also been demonstrated. With Cr(III) quenchers, in particular, where emission from the ^2E state is observed, intra- and intermolecular energy transfer has been established [6]. In covalently linked systems, energy transfer efficiency is a function of the strength of the electronic coupling between the centers, the linking molecules, and the distance between the donor and the acceptor portions of the complexes [7]. In the absence of a subsequent emission from the quencher, distinctions between energy transfer and electron transfer are often based on energy arguments. However, energy arguments and/or correlations between the bimolecular quenching rate constant and acceptor energy level, or redox potential, are often ambiguous. In the quenching of the MLCT states of Ru(II) and Os(II) diimines by molecular oxygen, for example, singlet oxygen formation is attributed to energy transfer, but an electron transfer process cannot be ruled out [6].

A third type of quenching mechanism, although far less common than energy- and electron-transfer processes, has been shown to occur in Ru(II) diimine complexes that possess acid–base sites on one or more of the ligands [8–16]. In these cases, optical excitation redistributes electron density in the complex, and the redistributed charge produces immense changes in acid–base properties. As a result, emission lifetime and intensity are pH dependent. In the complexes $(bpy)_2RuBL^{2+}$, where BL denotes the bridging ligands 2,3-bis(2-pyridyl)pyrazine (dpp) or [4,7]phenanthrolino[5,6]pyrazine (ppz), for example, optical excitation leads to an MLCT state localized on the BL ligand [4,17]. The normal modes resonant with the MLCT absorption showing the largest resonance enhancement indicate that the majority of the charge transferred in the formation of the luminescent MLCT state exists near the peripheral nitrogens. However, it is not clear whether the charge is symmetrically distributed between both nitrogens, or localized on a specific nitrogen. Nevertheless, optical excitation increases the electron density at these nitrogens, and this increase in electron density increases their basicity. In the time required for intersystems crossing to the luminescent state localized on the BL ligand, $\leqslant 100$ ps, the basicity of a peripheral nitrogen in $(bpy)_2Rudpp^{2+}$ increases by greater than four orders of magnitude, while the increase in $(bpy)_2Ruppz^{2+}$ is greater than five orders of magnitude [16]. Similar increases in basicity have been reported for other diimine complexes [8,9,12–16]. In each case, excitation increases the charge density in the ligand and the increased charge density increases basicity of a peripheral acid–base functionality by orders of magnitude.

The converse is also true, i.e. optical excitation produces decreases in basicity of similar magnitude. Population of the MLCT state of $(bpy)_2Ru(CN)_2$, for example, shifts charge density to the bpy ligand [8]. The optically induced polarization creates a more positive metal center that, in turn, inductively reduces the electron density on the cyano ligand thereby reducing its basicity [8]. In this case, the molecule is a stronger base in the ground state than it is in the excited state by approximately five orders of magnitude [8]. There is no thermal analogue to the changes in basicity induced optically, but it is clear that much smaller changes in acid–base properties can produce significant changes in thermal reactivity. If the changes in acid–base properties are immense, why is there no chemical manifestation of these changes? We believe the answer lies in the energy of the excited state, i.e. analogous to a photoredox process, the chemically induced changes are transient and have yet to be identified.

Here, we describe a series of experiments that indicate that there is indeed an excited state acid–base chemistry and this chemistry is the basis of another type of quenching mechanism. In those complexes where optical excitation changes the acid–base properties of the complex, bimolecular quenching results in an excited state acid–base chemistry that is expressed chemically as changes in coordination and nucleophilicity. Optical excitation of $(bpy)_2Rudpp^{2+}$, for example, increases the basicity of the peripheral nitrogens [16]. Evidence presented here indicates that the excited complex acts as a ligand and coordination to a second metal center leads to emission quenching. The result is an "associative" excited state coordination chemistry where, in contrast to the more common photoinduced degradation of a complex, the photochemical reaction increases the metal content of the complex. With $(bpy)_2Ru(CN)_2$, optical excitation decreases the basicity of the cyano group [8], and results obtained with $(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br^{2+}$ indicate that the excited state is indeed dissociative. In this case, the ground state is a stronger base than the excited state. Consequently, analogous to the complementary thermal reaction that regenerates the original reactants in a photoredox process, i.e. reaction (2), provided the dissociated $(bpy)_2Ru(CN)_2$ and $Rh(NH_3)_4Br^{2+}$ fragments do not diffuse out of the solvent cage, dissociation in the excited state is followed by re-association in the ground state to reform the thermodynamically stable, ground state bimetallic. Hence, the changes in coordination that occur in the excited state are transient, and in the absence of an appropriate secondary chemistry are not apparent. Nucleophilicity parallels basicity, and quenching experiments with reagents known to react with nucleophiles also exhibit a pattern of behavior consistent with an excited state nucleophilicity.

2. Experimental

2.1. Materials

$[(bpy)_2Rudpp](PF_6)$ was prepared by a previously described procedure and purified by column chromatography [4,17]. $(bpy)_2Ru(CN)_2$ and *trans*-

$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br](PF_6)_2$ were prepared and purified by literature methods [7,18]. K_2PtCl_6, K_2PdCl_6 and K_3RhCl_6 (Strem Chemical) were used as received since the electronic spectra of the complexes agreed with literature data [19]. CH_3I (Aldrich) was distilled prior to use to remove trace amounts of copper added as a stabilizer.

2.2. Photochemical procedures

Aqueous solutions containing $(bpy)_2Rudpp^{2+}$ and the metal chlorides were adjusted to an ionic strength of 3.0 M with NaCl and irradiated in previously described 1 cm cells with 488 nm light from an Ar^+ laser. The beam was expanded with a lens to a diameter sufficient to irradiate the entire solution volume, and the intensity within the cell was measured by ferrioxolate actinometry. Irradiations were generally carried out in air saturated solutions since, consistent with the short emission lifetime of $(bpy)_2Rudpp^{2+}$, 135 ± 14 ns [16], results obtained in air saturated solutions did not differ beyond experimental error from those obtained with solutions degassed by freeze–pump–thaw cycles. UV–visible spectra were recorded periodically during the photochemical reaction, and the rate of appearance of the bimetallic was determined from the appearance of the lower energy MLCT transition characteristic of bimetallic complex.

2.3. Physical measurements

Electronic spectra were recorded a Perkin–Elmer Model 8452 diode array spectrometer, or an Aviv Model 14 spectrometer. Emission spectra and emission quenching were measured on a Spexs Model 1681 emission spectrometer equipped with a Hamamatsu R928 red-sensitive photomultiplier. Emission lifetimes were determined by monitoring the emission decay following 535 nm excitation from a Nd:YAG laser [17]. Emission decays were recorded over a time range corresponding to three to five lifetimes, and first order plots of the emission intensity, both in the presence and absence of the hexachlorides, gave no indication of non-linearities indicative of a faster or slower decay component.

3. Results and discussion

$Ru(bpy)_2(dpp)^{2+}$ and $Ru(bpy)_nBL_{3-n}^{2+}$ (BL denotes a diimine bridging ligand) complexes in general have been widely used to assemble polymetallic complexes [4,17,20–22]. 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 $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$. The shift to longer wavelength has been observed in all reactions involving coordination of a second metal to the dpp peripheral nitrogens, and in those cases where the charge transfer is ultimately to the bridging ligand, it is characteristic of the formation of a polymetallic complex. The thermal reaction leading to the formation of $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ was measured spectrophotometrically in aqueous solution at an ionic strength of 1.0 M (NaCl). At 30 °C, the rate law for the thermal reaction is $R=k_{th}[Ru(bpy)_2(dpp)^{2+}]^{0.7\pm0.2}[PtCl_6^{2-}]^{0.8\pm0.2}$, where $k_{th}=1.8\pm0.4\times10^{-4}\ M^{-1}\ s^{-1}$. In the 30 to 50 °C range, the temperature dependence of the rate yields an activation energy, E_a, of 15 ± 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 $PtCl_6^{2-}$ (Fig. 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 (Fig. 1) indicate a quantitative conversion through ⩾60–70% reaction. Similar spectral changes indicative of dimer formation occur with $RhCl_6^{3-}$ and $PdCl_6^{2-}$. With both complexes, the spectroscopic data reveal quantitative conversions to the bimetallic, although with $PdCl_6^{2-}$ the extent of the spectroscopically measurable quantitative conversion is limited to 20% by the hydrolysis of the hexachloride.

At low ionic strength, or very high concentrations of the hexahalide, quenching experiments (Fig. 2) clearly show that the quenching process and the subsequent chemistry are dominated by ion-pair formation. This discussion focuses on the data obtained at high ionic strength, $\mu=3.0$ M (NaCl), where the agreement between the

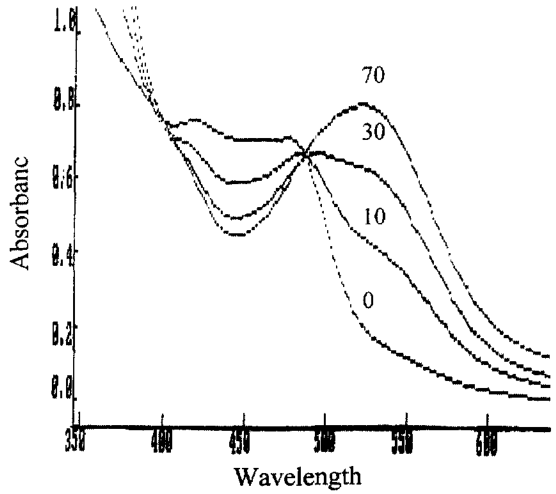

Fig. 1. Spectral changes during a 450 nm photolysis of a 10^{-4} M $Ru(bpy)_2(dpp)^{2+}$ and 10^{-3} M $PtCl_6^{2-}$ solution. Numbers refer to irradiation times in seconds.

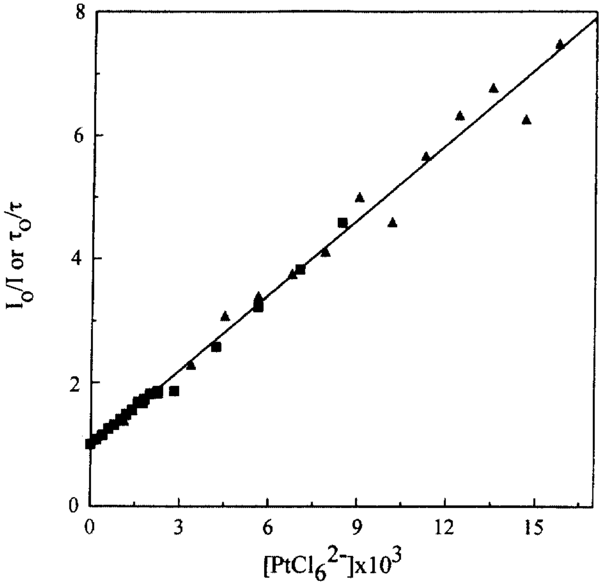

Fig. 2. Intensity (■) and lifetime (△) quenching of the 675 nm emission of $Ru(bpy)_2(dpp)^{2+}$ by $PtCl_6^{2-}$, $\mu=3.0$ M (NaCl).

intensity, $403 \pm 35\ M^{-1}$, and lifetime, $397 \pm 43\ M^{-1}$, quenching establishes a diffusion controlled process (Fig. 2). At $\mu=3.0$ M (NaCl), the Stern–Volmer constants from intensity and lifetime quenching of the 675 nm emission of $Ru(bpy)_2(dpp)^{2+}$ by $PtCl_6^{2-}$ are also in excellent agreement with the Stern–Volmer constant, $413 \pm 62\ M^{-1}$, 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}, vs. the reciprocal of the concentration of $PtCl_6^{2-}$ (Fig. 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 Fig. 3 yields a limiting value of Φ_{bi} of 0.18 ± 0.02, and taking 135 ± 14 ns as the lifetime of the MLCT state of $Ru(bpy)_2(dpp)^{2+}$ [16], 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 as previously noted, the reaction occurs via optical excitation of $[Ru(bpy)_2(dpp)^{2+}, PtCl_6^{2-}]$ ion pairs.

The excited state energies and the redox potentials of the different complexes indicate that formation of the bimetallic does not involve either photoinduced electron or energy transfer. The emission from $Ru(bpy)_2(dpp)^{2+}$ places the MLCT state, which is 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 [19]. Lower energy, weaker absorptions of $PtCl_6^{2-}$ place the spin forbidden $^3T_2$ state at 2.8 eV [19]. An absorption corresponding to the transition to the $^3T_1$ state is not evident in the spectrum of $PtCl_6^{2-}$. Taking 2.8 eV as the energy of the $^3T_2$, however,

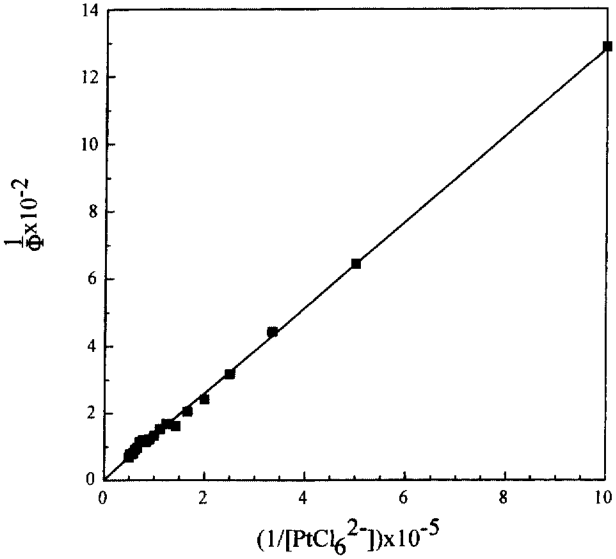

Fig. 3. Reciprocal of the quantum yield of $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formation as a function of the reciprocal of the $PtCl_6^{2-}$ concentration, $\mu = 3.0$ M (NaCl).

the Tanabe–Sugano diagram indicates that $^3T_1$ state lies 2 eV above the ground state. Clearly, uncertainties exist in the latter, yet neither state is expected to be $\leqslant 1.48$ eV making energy transfer endergonic. Nor is the reaction 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 $\geqslant 90\%$ of the excitation is absorbed by $Ru(bpy)_2(dpp)^{2+}$, direct photolysis of $PtCl_6^{2-}$ at best accounts for $\leqslant 20\%$ of the $[Ru(bpy)_2(dpp)PtCl_4]^{2+}$ formed. [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.] Nevertheless, the high quantum yield of $PtCl_6^{2-}$ decomposition makes trivial effects bothersome and additional competitive quenching experiments were carried out to establish that the reaction occurs via excitation of $Ru(bpy)_2(dpp)^{2+}$. Competitive quenching by Fe(III), which reduces bimetallic formation to $\Phi_{bi} \leqslant 10^{-5}$, further establishes that formation of the bimetallic occurs via excitation of $Ru(bpy)_2(dpp)^{2+}$, 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 ΔH_f° of $PtCl_{3(s)}$ suggests that oxidative quenching:

$$^*Ru(bpy)_2(dpp)^{2+} + PtCl_6^{2-} \rightarrow Ru(bpy)_2(dpp)^{3+} + Pt(III) \qquad (5)$$

is endergonic by as much as 4 eV [23]. Reductive quenching seems equally unlikely since it would yield the unlikely oxidation state Pt^{5+}. Similar estimates of the reduction potentials of $RhCl_6^{3-}$ and $PdCl_6^{2-}$ suggest that one-electron reductions are also endergonic [23].

To further test the possibility of bimetallic formation via an electron or energy transfer mechanism, a number of experiments were carried out in aqueous solution, $\mu = 1.0$ M (NaCl), using the chlorides salts of Fe^{3+}, Co^{3+} and Cr^{3+} as quenchers. Fe^{3+} was chosen because it is a known electron transfer quencher. Oxidative quenching of $^*Ru(bpy)_2(dpp)^{2+}$ to form Fe^{2+} is exergonic by 1.0 eV, and both Fe^{3+} and Fe^{2+} form stable complexes with diimine ligands. The reduction potential of Co^{3+}, $Co^{3+} + e^- \rightarrow Co^{2+}$, 1.84 V (3 N HNO_3) [24] suggests that quenching might occur by energy transfer. Cr^{3+} is known to quench by an energy transfer process, and like Co^{3+} is thermally substitution inert. Consequently, if energy transfer were to occur and form a coordinatively unsaturated species with both Co^{3+} and Cr^{3+}, coordination to the peripheral nitrogens of dpp is expected to produce a thermally stable product. Nevertheless, bimetallic formation does not occur, $\Phi_{bi} \leqslant 10^{-3}$, with each of these transition metal ions.

Mechanistic distinctions based on energies and calculated efficiencies are fraught with uncertainties, and by themselves do not conclusively preclude energy or electron transfer processes. Central to the electron and energy transfer processes, however, 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 amounts of coordinated water. With $PtCl_6^{2-}$ 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 energetics of the processes, along with the specificity of the formation of the bimetallic, supports the interpretation of an excited state coordination chemistry.

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 $\geqslant 10^3$ relative to the ground state [16]. We propose that this immense increase in basicity, rather than energy or electron transfer, leads to coordination of the second metal ion. Since the increase in basicity exists only in the excited state, coordination to the second metal is viewed as exiplex formation, where the increased electron density at the peripheral nitrogens enhances a coordinate covalent interaction between one peripheral nitrogen and the platinum ion. 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 to form the thermodynamically stable bimetallic in which the dpp bridging ligand is bidentate with both metal centers.

In the above case, which we present as an example of an "associative" excited state coordination chemistry, the complex acts as a ligand, and optical excitation increases its basicity leading to coordination to a second metal center. As noted in the Introduction, optical excitation of $(bpy)_2Ru(CN)_2$ reduces the basicity of the cyanide ion by ca. five orders of magnitude [8], and we have begun to explore the possibility of the converse to an associative coordination chemistry, i.e. optical excitation decreases the basicity of the coordinating ligand resulting in a dissociative excited state. In the bimetallic complex *trans*-$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$, $(bpy)_2Ru(CN)_2$ can be viewed as a ligand coordinated to Rh(III) via cyanide. The visible spectrum of $(bpy)_2Ru(CN)_2$ consists of an absorption with a maximum at 465 nm and a shoulder at shorter wavelength which is assigned to an MLCT transition terminating in the bipyridine ligand. *Trans*-$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ exhibit a visible spectrum very similar to that of $(bpy)_2Ru(CN)_2$ except that the band maximum shifts to 420 nm. The shift to shorter wavelength indicates that, although a positive metal center is attached to the CN, the optical transition continues to be a MLCT transition terminating in the bipyridine ligand as opposed to terminating in the cyanide ligand. As pointed out by Demas and coworker, population of the MLCT state of $(bpy)_2Ru(CN)_2$ reduces the basicity of the cyanide group by ca. five-orders of magnitude [8]. Since the electronic spectrum of *trans*-$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ is dominated by the MLCT transition of $(bpy)_2Ru(CN)_2$, population of an MLCT state localized on the $(bpy)_2Ru(CN)_2$ moiety would be expected to decrease the basicity of the bridging cyanide. Hence, optical excitation of *trans*-$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ might be expected to result in a dissociative excited state, i.e.

$$[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+} \rightarrow [{}^*(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}] \tag{6}$$

where $[{}^*(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}]$ denotes the excited ruthenium complex and the dissociated rhodium fragment within the solvent caged. The caged pair relaxes by non-radiative decay to the ground state molecules:

$$[{}^*(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}] \rightarrow [(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}] + \text{heat} \tag{7}$$

with a corresponding ca. five order of magnitude increase in the basicity of the cyanide of $(bpy)_2Ru(CN)_2$. Provided one of the relaxed pair does not diffuse from the solvent cage, the complexes bind back together due to the large increase in basicity of the $(bpy)_2Ru(CN)_2$:

$$[(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}] \rightarrow [(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+} \tag{8}$$

As with a photoinduced redox process, the chemical change is transient and not readily apparent. A scavenger, such as H^+, however, could intercept the dicyano prior to recoupling:

$$[(bpy)_2Ru(CN)_2,\ Rh(NH_3)_4Br^{2+}] + H^+ \rightarrow (bpy)_2Ru(CN)(CNH)^+ + Rh(NH_3)_4Br(H_2O)^{2+} \qquad (9)$$

while the coordinatively unsaturated $Rh(NH_3)_4Br^{2+}$ would be expected to form $Rh(NH_3)_4Br(H_2O)^{2+}$ in aqueous solution. As a result, the quantum yield of $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ decomposition would be expected to increase with decreasing pH and yield, after neutralization, $(bpy)_2Ru(CN)_2$ and $Rh(NH_3)_4Br(H_2O)^{2+}$. Although the number of points is small, the quantum efficiency of decomposition clearly increases with decreasing pH (Fig. 4). Spectroscopic analysis after neutralization and separation of the photoproducts by cation exchange chromatography confirms the presence of $(bpy)_2Ru(CN)_2$ and a Rh(III) amine product. Concurrent experiments show that thermal decomposition cannot account for the observed pH dependence. The thermal rate of decomposition of $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ in aqueous solution is 1.9×10^{-12} mol/l s, while that in 0.5 M H_2SO_4 is 6.3×10^{-12} mol/l s. Further experiments are needed to establish the nature of the rhodium complex. Nevertheless, the results gathered to date are consistent with the expected excited state acid–base behavior of $(bpy)_2Ru(CN)_2$ and are presented as an example of a dissociative excited state coordination chemistry.

Nucleophilicity parallels basicity, and we have begun a series of experiments to explore the possibility of excited state nucleophilicity. Our results are limited to

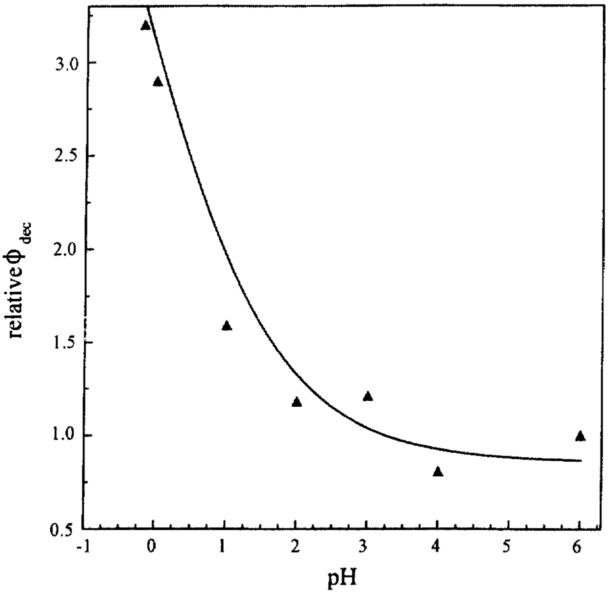

Fig. 4. The relative quantum yield of decomposition of $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ as a function of pH.

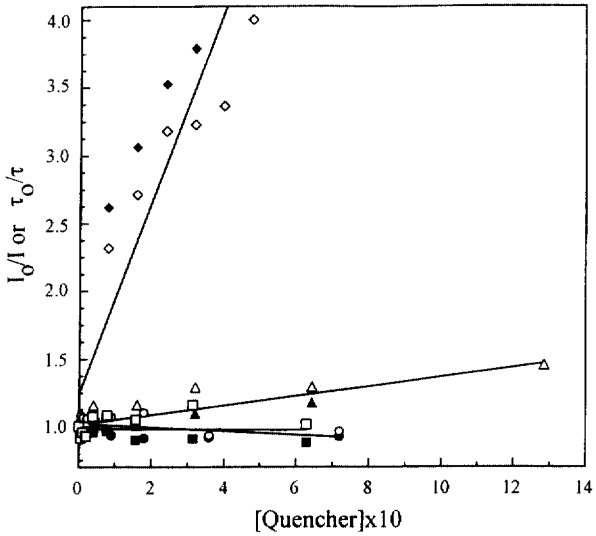

Fig. 5. Quenching of $Ru(bpy)_2(dpp)^{2+}$ in acetonitrile solution by reagents that do and do not undergo nucleophilic addition reactions. Solid and hollow symbols indicate intensity and lifetime data: methyl tosylate (◆, ◇); methyl iodide (▲, △); o-iodotoluene (■, □); iodobenzene (●, ○).

emission quenching, but as illustrated in Fig. 5, quenching of $^*Ru(bpy)_2(dpp)^{2+}$ by tosylate and methyl iodide is consistent with the occurrence of excited state nucleophilicity. High concentrations of tosylate and methyl iodide are needed to see quenching, but the results are not simply due to a solvent effect. Increasing the organic component of the solvent generally increases the emission intensity and lifetime of Ru(II) diimines. Consequently, a solvent effect is expected to produce a negative Stern–Volmer constant. Because of the endergonicity associated with the loss of the resonance stabilization, iodobenzene and iodotoluene do not undergo nucleophilic attack, and consistent with the expected solvent effect yield negative Stern–Volmer constants. The quenching patterns are small, but the quenching pattern is consistent with an excited state nucleophilicity.

4. Conclusion

The energetics of quenching of $Ru(bpy)_2(dpp)^{2+}$ by $PtCl_6^{2-}$, $RhCl_6^{3-}$ and $PdCl_6^{2-}$ and the specificity of formation of the corresponding bimetallics suggest that quenching does not occur by electron or energy transfer, but rather by means of an excited state coordination chemistry arising from the immense increase in basicity that occurs on population of the $Ru(bpy)_2(dpp)^{2+}$ MLCT state. In contrast to this chemistry, where optical excitation increases basicity of the peripheral nitrogen of dpp leading to an associative coordination reaction, population of the MLCT state of $(bpy)_2Ru(CN)_2$ decreases basicity, and pH dependence of the quantum yield of decomposition of $[(bpy)_2Ru(CN)(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$ suggests that optical excitation leads to a dissociative excited state coordination chemistry. Obviously additional work needs to be done, but data gathered here suggest that, in addition to electron and energy transfer, the immense changes in acidity and basicity that occur on excitation of certain Ru(II) diimine complexes results in an excited state acid–base chemistry, where quenching occurs by changes in coordination and nucleophilicity. Under certain circumstances the changes are transient, but as with excited state electron transfer chemistry, the transient nature of the chemistry offers the potential of using pulsed lasers as a relaxation technique to explore ligand substitution chemistry in previously unaccessible time domains.

Acknowledgements

The authors thank Professors William Hersh and William Berkowitz for their comments and questions that helped to develop and refine these ideas. Support of this research by the National Science Foundation (DMR-9314033), DOD/AFSOR (F49620-94-1-0209), the New York State Center for Advanced Technology at the City University of New York, the Howard Hughes Foundation, and the Research Foundation of the City University of New York is gratefully acknowledged.

References

[1] H.D. Gafney, A.W. Adamson, J. Am. Chem. Soc. 94 (1972) 8238.
[2] K. Kalyanasundram, Coord. Chem. Rev. 46 (1982) 159.
[3] V. Balzani et al., Coord. Chem. Rev. 84 (1988) 85.
[4] H.D. Gafney, Y. Fuchs, S. Lofters, T. Deiter, S. Wei, R. Morgan, T.C. Strekas, A.D. Baker, J. Am. Chem. Soc. 109 (1987) 2691.
[5] H.D. Gafney, R. Berkoff, K. Krist, Inorg. Chem. 19 (1980) 1 and references cited therein
[6] J.N. Demas, E.W. Harris, R.P. McBride, J. Am. Chem. Soc. 99 (1977) 3547.
[7] Y. Lei, T. Buranda, J.F. Endicott, J. Am. Chem. Soc. 112 (1990) 8820.
[8] S.H. Peterson, J.N. Demas, J. Am. Chem. Soc. 98 (1976) 7880.
[9] R.J. Crutchley, N. Kress, A.B.P. Lever, J. Am. Chem. Soc. 105 (1983) 1170.
[10] P.J. Giordano, C.R. Bock, M.S. Wrighton, L.V. Interrante, J. Am. Chem. Soc. 99 (1977) 3187.
[11] P.J. Giordano, C.R. Bock, M.S. Wrighton, L.V. Interrante, J. Am. Chem. Soc. 100 (1978) 6960.
[12] J. Fergeson, W.H.F. Sasse, Chem. Phys. Lett. 68 (1979) 21.
[13] J. Fergeson, W.H.F. Sasse, Inorg. Chem. 23 (1984) 4123.
[14] T. Shimidzu, T. Iyoda, K. Izaki, J. Phys. Chem. 89 (1985) 642.
[15] D.P. Rillema, G. Allen, T.J. Meyer, Inorg. Chem. 22 (1983) 1617.
[16] H.D. Gafney, W. Hosek, S.A. Tysoe, A.D. Baker, T.C. Strekas, Inorg. Chem. 28 (1989) 1228.
[17] H.D. Gafney, C. Braunstein, A.D. Baker, T.C. Strekas, Inorg. Chem. 23 (1984) 857.
[18] G.M. Bryant, J.E. Fergeson, H.K.E. Powell, Aust. J. Chem. 24 (1971) 257.
[19] D.S. Martin, Adv. Chem. Ser. 98 (1971) 74.
[20] K.J. Brewer, W.R. Murphy, S.R. Spurlin, J.D. Petersen, Inorg. Chem. 25 (1986) 882.
[21] W.R. Murphy, K.J. Brewer, G. Gettliffe, J.D. Petersen, Inorg. Chem. 28 (1989) 81.

[22] J.D. Petersen, W.R. Murphy, K.J. Brewer, K.R. Ruminski, Coord. Chem. Rev. 64 (1985) 261.

[23] A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985, pp. 344, 413.

[24] A.J. Bard, L.R. Falkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, 1980, p. 700.