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A Simple Photochemical Synthesis of Some Bis(bipyridyl)ruthenium(II) Complexes

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Existing methods for the synthesis of bis(2,2'-bipyridine) complexes of ruthenium(II) are often quite tedious. General methods for producing $[Ru(bpy)_2X_2]$ or $[Ru(bpy)_2XY]$ complexes most commonly rely on chloride displacement from $[Ru(bpy)_2Cl_2]$.[1-6] This compound may be prepared through the pyrolysis or reduction of $(bpyH)[Ru(bpy)Cl_4]$,[7] which in turn may be prepared from $K_2[RuCl_5(H_2O)]$.[7,8] The latter compound is not generally available but may be prepared from RuO_2.[9]

A second route to $[Ru(bpy)_2Cl_2]$ proceeds by heating $[Ru(bpy)_3]Cl_2$ with powdered silica under vacuum.[10] We have found that this preparation leaves a variety of complexes on the silica, and separation is difficult.

More recently $[Ru(bpy)_2CO_3]$ has been used as a general intermediate.[6,11] It too, however, is prepared from $[Ru(bpy)_2Cl_2]$.[11] The oxalato complex $[Ru(bpy)_2(ox)]$, which can be prepared directly from $K[RuCl_5(H_2O)]$[10] or K_2RuCl_6,[12] has also been used to synthesize $[Ru(bpy)_2(CN)_2]$.[12] This compound has also been produced directly from $K_2[Ru-$

$Cl_5(H_2O)]$ in aqueous solution.[13]

While studying the substitutional photochemistry of $[Ru(bpy)_3]^{2+}$, we reported a photochemical synthesis of $[Ru(bpy)_2(NCS)_2]$[14] and $[Ru(bpy)_2Br_2]$.[15] The procedure can be extended to other complexes. It is simple and direct and makes use of the low solubility of some of the $[Ru(bpy)_2X_2]$ complexes in ethanol or water.

Unfortunately, $[Ru(bpy)_2Cl_2]$ is not easily prepared this way. It is quite soluble in alcohols and is substitutionally labile in water. Still, it is possible that one or another of the complexes which can be produced photochemically may be usable as a general precursor to other complexes.

Experimental Section

To prepare $[Ru(bpy)_2X_2]$, we used $[Ru(bpy)_3]X_2$ as starting material, although, in general, satisfactory results could be obtained with $[Ru(bpy)_3]Cl_2$ and a stoichiometric excess of a salt of the anion X^-. $[Ru(bpy)_3]X_2$ was prepared from $[Ru(bpy)_3]Cl_2$ by ion-exchange chromatography, utilizing 5% or less of the total resin capacity (Dowex 1-X8).

$[Ru(bpy)_2I_2]$ and $[Ru(bpy)_2(NO_2)_2]$, which are only very slightly soluble in ethanol, were prepared by dissolving the corresponding $[Ru(bpy)_3]^{2+}$ salt in ethanol (15 mL), placing the solution in a 5-cm quartz spectrophotometer cell, deoxygenating by bubbling N_2 through the cell for 15 min, and irradiating the cell for 4 h with a 500-W mercury lamp. The black (iodo) or golden (nitro) crystals which formed were filtered, washed with boiling ethanol, and dried in vacuo. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2I_2] \cdot C_2H_5OH$: C, 37.04; H, 3.11; I, 35.58. Found: C, 37.04, 37.79; H, 2.35, 2.78; I, 34.71. Calcd for $[Ru(C_{10}H_8N_2)_2(NO_2)_2] \cdot 1.5H_2O$: C, 45.11; H, 3.60; N, 15.79. Found: C, 44.89, 45.40; H, 3.66, 3.73; N, 15.49, 15.94.

A number of anions yielded complexes which are soluble in ethanol and methanol but insoluble in water. $[Ru(bpy)_2(N_3)_2]$, $[Ru(bpy)_2(mal)]$, where mal = malonate, and $[Ru(bpy)_2(CN)_2]$ fall into this category. The procedure followed was to photolyze the corresponding $[Ru(bpy)_3]X_2$ salt in ethanol for 4 h as before and then dilute the resulting photolysate with an equal volume of H_2O. Black (malonato and azido) or red (cyano) crystals formed upon cooling overnight, which were washed with water and dried in vacuo. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(N_3)_2] \cdot 1.5H_2O$: C, 45.79; H, 3.65; N, 26.71. Found: C, 45.84; H, 3.45; N, 25.91. Calcd for $[Ru(C_{10}H_8N_2)_2(C_3H_2O_4)] \cdot 2.5H_2O$: C, 49.28; H, 4.14; N, 10.00. Found: C, 49.30; H, 4.18; N, 10.08. Calcd for $[Ru(C_{10}H_8N_2)_2(CN)_2] \cdot 3.5H_2O$: C, 49.99; H, 4.39; N, 15.90. Found: C, 50.19; H, 4.36; N, 15.47. Our yields were generally in the range of 15–35% with 4-h irradiation times, but the unreacted starting material could be reused.

For those anions which form bis(bipyridine) complexes which do not crystallize from ethanol or water, the complexes may still be obtained photolytically by subjecting the photolysate (in ethanol) to Sephadex LH-20 chromatography, where the tris complex is generally eluted first. The eluant containing the bis complex may be evaporated to yield the solid product. This method may be more tedious, however, than standard synthetic procedures.

Unexpected products were obtained upon photolysis of $[Ru(bpy)_3]^{2+}$ salts with IO_3^- and $SeCN^-$ as counterions, indicating that the substitution reaction may not be as straightforward as it appears to be. In both cases a product crystallized directly from ethanol solution.

The product from photolysis of $[Ru(bpy)_3](IO_3)_2$ in ethanol was $[Ru(bpy)_2I_2]$. This is at least reasonable, since the excited-state $[Ru(bpy)_3]^{2+}$ complex is thermodynamically capable of reducing IO_3^-,[16] while the resulting $[Ru(bpy)_3]^{3+}$ could oxidize the solvent. How the iodate reduction and the bipyridine substitution are related is not yet clear.

The selenocyanate case is more baffling. Because of the chemical similarity to thiocyanate, it was assumed that an analogous product would be formed, $[Ru(bpy)_2(NCSe)_2]$. Analysis revealed, however, that the black crystalline product obtained contained no selenium and was consistent with its formulation as $[Ru(bpy)_2(N_3)_2]$. Anal. Calcd for $[Ru(C_{10}H_8N_2)_2(N_3)_2]$: C, 48.28; H, 3.24; N, 28.16. Found: C, 48.01; H, 3.45; N, 27.58.

Among the unusual features associated with this reaction is the direct crystallization of the product from ethanol, with no solvent of crystallization. With azide present from the outset, water had to be added to induce crystallization, which occurred with 1.5 water molecules per complex.

Infrared spectroscopy was used for further confirmation of azido coordination. The asymmetric N–N stretching frequency, expected between 2000 and 2100 cm⁻¹, cannot be used, since selenocyanate would exhibit a C–N stretch in the same region. However, the symmetric N–N stretching frequency is expected between 1240 and 1280 cm⁻¹,[17,18] with no counterpart in the selenocyanate or bipyridine spectrum. A band was observed at 1246 cm⁻¹, which would appear to be the ν_5(N–N–N) mode.

The selenocyanate reaction in particular, and [Ru(bpy)₃]²⁺ photosubstitution reactions in general, appears to merit additional investigation aimed at unraveling both mechanistic and overall stoichiometric details of the process.

Registry No. [Ru(bpy)₃]Cl₂, 14323-66-9; [Ru(bpy)₃]I₂, 23792-07-6; [Ru(bpy)₃](NO₂)₂, 71031-49-7; [Ru(bpy)₃](mal), 71000-88-9; [Ru(bpy)₃](N₃)₂, 71000-89-0; [Ru(bpy)₃](CN)₂, 71050-17-4; [Ru(bpy)₃](SeCN)₂, 71031-52-2; [Ru(bpy)₃](IO₃)₂, 71000-90-3; Ru(bpy)₂I₂, 71048-70-9; Ru(bpy)₂(NO₂)₂, 29241-01-8; Ru(bpy)₂(N₃)₂, 55124-48-6; Ru(bpy)₂(mal), 71000-91-4; Ru(bpy)₂(CN)₂, 20506-36-9.

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The [Co(NH₃)₅(O₂C⁻·)]²⁺ Coordinated Ligand-Radical Complex[1]

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One of the first coordinated ligand-radical species to be proposed in electron-transfer reactions was [Co(NH₃)₅(O₂C⁻·)]²⁺ which was postulated by Candlin and Halpern[2] as an intermediate in the MnO₄⁻ oxidation of Co(NH₃)₅O₂CH²⁺ in aqueous solution. They interpreted their observations in terms of intramolecular electron transfer in the coordinated ·CO₂⁻ complex to form Co²⁺ (aq) and CO₂ in competition with reaction with MnO₄⁻ to form Co(NH₃)₅OH₂³⁺ and CO₂. The ratio of the rate constants of these reactions was evaluated but their absolute values were not determined.

Because of the efficient reactions of OH radicals and H atoms with HCO₂H ($k = 1.5 \times 10^8$ and 1.1×10^6 M⁻¹ s⁻¹)[3,4] and HCO₂⁻ ($k = 2.0 \times 10^9$ and 5.0×10^7 M⁻¹ s⁻¹)[3,4] to form ·CO₂⁻, we reasoned that OH and H should react with Co(NH₃)₅O₂CH²⁺ via H abstraction to form [Co(NH₃)₅(O₂C⁻·)]²⁺. In this way we could test whether or not [Co(NH₃)₅(O₂C⁻·)]²⁺ engages in intramolecular electron transfer, evaluate the rate constants for the various processes, and

provide insight into the mechanism of induced electron transfer in which an oxidizing agent causes the reduction of the metal center.[5]
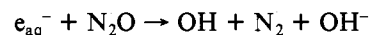
Experimental Section

[Co(NH₃)₅O₂CH](ClO₄)₂ was prepared according to the method of Sebera and Taube;[6] the spectral characteristics of the compound were identical with those reported in the literature.

Pulse radiolyses with optical absorption detection were conducted by using the apparatus at the U.S. Army Natick Research and Development Command;[7] pulse radiolyses with kinetic conductivity detection were performed at the Radiation Laboratory of the University of Notre Dame.[8] Continuous radiolyses were conducted at Boston University in ⁶⁰Co γ-ray sources (dose rates ∼3.5 × 10¹⁶ and ∼7.0 × 10¹⁷ eV mL⁻¹ min⁻¹); the Fricke dosimeter[9] was used to evaluate the exact radiation dose received by the solutions.

The solutions were purged of air by saturation with N₂O (2.5 × 10⁻² M); alternatively, the solutions were saturated with O₂ (1.3 × 10⁻³ M). Reagent grade chemicals and Millipore water were used to prepare the solutions. Kitson's method[10] was used for the analysis of Co²⁺(aq). UV–vis spectra were determined with a Cary 118 spectrophotometer.

Results and Discussion

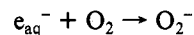The radiolysis of water and aqueous solutions proceeds according to the overall reaction H₂O ⟶ e⁻aq (2.8), OH (2.8), H (0.55) where the numbers in parentheses represent the G values (number of radicals formed/100 eV of energy absorbed) of the species. N₂O, H⁺, and O₂ are effective scavengers for e⁻aq;[11] H and ·CO₂⁻ also react with O₂.[4]

$$e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$$
$$(k = 8.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$$

$$e_{aq}^- + H^+ \rightarrow H$$
$$(k = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$$

$$e_{aq}^- + O_2 \rightarrow O_2^-$$
$$(k = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$$

$$H + O_2 \rightarrow HO_2$$
$$(k = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$$

$$HO_2 \rightleftharpoons H^+ + O_2$$
$$(pK_a = 4.8)^{12}$$
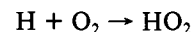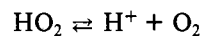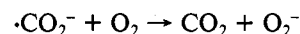
$$\cdot CO_2^- + O_2 \rightarrow CO_2 + O_2^-$$
$$(k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{13}$$

The pulse radiolysis (optical absorption) of buffered N₂O-saturated solutions of 5.0 × 10⁻⁴ M Co(NH₃)₅O₂CH²⁺ (pH 1–7) reveals pseudo-first-order bleaching of the substrate absorbance in the microsecond time frame corresponding to a second-order disappearance with $k \sim 2 \times 10^9$ M⁻¹ s⁻¹; no other transient or permanent absorbances are observed.[14] Continuous radiolysis under the same conditions produces Co²⁺(aq) in quantitative yield ($G = 6.1 \pm 0.3$) independent of pH, radiation dose, [substrate], and [phosphate buffer]; the absorption spectra of the radiolyzed solutions show loss of substrate stoichiometric with the formation of Co²⁺(aq). The pulse radiolysis (kinetic conductivity) of 5.0 × 10⁻⁴ M Co(NH₃)₅O₂CH²⁺ at pH 4.3 reveals that the full yield of Co(III) is generated within 2 μs as evidenced by the uptake of H⁺ from the release of NH₃. In fact, the results are very similar to those obtained for the reaction of e⁻aq with Co(NH₃)₅Cl²⁺.[15] The release of two ammonias, and presumably the nonammonia ligand, occurs with $t_{1/2} < 2$ μs; the fourth, fifth, and sixth ligands are released with $t_{1/2} = 8$, 80, and 500 μs, respectively.

The results demonstrate that the reaction of OH radicals and H atoms with Co(NH₃)₅O₂CH²⁺ leads quantitatively to Co²⁺(aq) and that the primary intermediate from the radical interaction has a lifetime toward the generation of Co(II) of ≤2 μs. The sequence of events given in eq 1–7 can be written