Electrogenerated chemiluminescence. 42. Electrochemistry and electrogenerated chemiluminescence of the tris(2,2'-bipyrazine)ruthenium(II) system
Jaime Gonzales-Velasco, Israel Rubinstein, R. J. Crutchley, A. B. P. Lever, and Allen J. Bard

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The electrochemical behavior and electrogenerated chemiluminescence (ecl) of Ru(bpy)$_3^{2+}$ (as the PF$_6^-$ salt) in acetonitrile solutions were investigated. Oxidation to the 3+ form and reduction to the 1+, 0, 1-, and 2- forms occur at potentials about 0.5 V more positive than those for the corresponding bipyridine complex. Emission characteristic of Ru(bpy)$_3^{2+}$ is produced upon the electron-transfer reaction between the 3+ and 1+ species. Weak emission also results from the reaction of the 3+ species with solvent or impurities. A comparison of the ecl efficiency between the bpy and its spectroscopic and photocatalytic properties suggested a study of the electrochemical and ecl behavior of this compound. Previous studies of Ru(bpy)$_3^{2+}$ showed that ecl is produced by the redox reaction between the 1+ and 3+ species as well as by reaction of the 3+ species with a number of reductants (e.g., especially oxalate). We were particularly interested in Ru(bpy)$_3^{2+}$ because the redox processes are shifted by ~0.5 V towards more positive potentials, compared with those for Ru(bpy)$_2^{3+}$. This could prove valuable in ecl in aqueous media where proton reduction interferes at negative potentials.

**Introduction**

Of the numerous compounds that produce chemiluminescence upon the electron-transfer reactions of electrogenerated species (ecl), that observed with the Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) system is among the most intense and best characterized.

**Note Added in Proof.** Since submission of this paper, several hardware improvements have allowed more sophisticated $^{183}$W NMR experiments to be performed. A two-dimensional $^{183}$W[2P] INADEQUATE spectrum of Li$_7$[Ti$_2$W$_6$O$_{19}$] has been obtained (Figure 6) and provides an unambiguous measure of the coupled sites without requiring accurate measurement of coupling patterns. Data are presented as a contour plot. Projection of the data onto the F$_2$ dimension (horizontal) shows a normal spectrum of pairwise $^{183}$W-O-$^{183}$W isopomers, while the second dimension (F, vertical) disperses those coupled peaks on the basis of the sum of the chemical shifts involved. The magnitudes of the couplings are retained so simple inspection of the contour pattern shows A coupled to B (edge), B to C (corner), C to D (edge), D to A (corner), and C to D (corner). The C-D edge connection is not observed, but both lines of the second-order C-D corner coupling are obvious.

Brevard and Schimpf$^{13}$ have also applied similar sophisticated two-dimensional methods to determining W-W connectivities in heteropolytungstates.

**Chemiluminescence of the Tris(2,2'-bipyridine)ruthenium(II) System**

JAIME GONZALEZ-VELASCO$^{1,6}$, ISRAEL RUBINSTEIN$^{1,1}$, R. J. CRUTCHLEY$^{1,1}$, A. B. P. LEVER$^{1,1}$, and ALLEN J. BARD$^{1,14}$

Received April 12, 1982

The chemical name of the compound is Ruthenium(II) tris(2,2'-bipyridine) chloride (Ru(bpy)$_3^{2+}$Cl$^-$).

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**Introduction**

Of the numerous compounds that produce chemiluminescence upon the electron-transfer reactions of electrogenerated species (ecl), that observed with the Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine) system is among the most intense and best characterized.$^{24}$ A recent report$^1$ of a new, related compound,

Ru(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine)

and its spectroscopic and photocatalytic properties suggested a study of the electrochemical and ecl behavior of this compound. Previous studies of Ru(bpy)$_3^{2+}$ showed that ecl is produced by the redox reaction between the 1+ and 3+ species as well as by reaction of the 3+ species with a number of reductants (e.g., especially oxalate).$^{24}$ We were particularly interested in Ru(bpy)$_3^{2+}$ because the redox processes are shifted by ~0.5 V towards more positive potentials, compared with those for Ru(bpy)$_2^{3+}$. This could prove valuable in ecl in aqueous media where proton reduction interferes at negative potentials. A comparison of the ecl efficiency between the bpz

$^{24}$ See ref 24.
and bpy complexes is also of interest.

In this paper we describe the electrochemical behavior of the Ru(bpz)$_2$$^{2+}$ system in acetonitrile (MeCN) solutions and demonstrate the production of ecl and its characteristics.

Experimental Section

**Chemicals.** Ru(bpz)$_2$$^{2+}$ was obtained in the form of the PF$_6$- salt. It was recrystallized from MeCN and dried for 24 h under vacuum at room temperature. The tetra-n-butylammonium hexafluorophosphate (TBAFP) used as supporting electrolyte was prepared by the reaction of NH$_4$PF$_6$ (Ozark-Mahoning) and tetra-n-butylammonium perchlorate (Aldrich). The precipitate of TBAFP was obtained, washed and repeatedly washed with distilled water. The precipitate was dissolved in boiling EtOH; when the solution was cooled, TBAFP was obtained in the form of small crystals. This procedure was repeated three times. Finally the crystals were recrystallized from a mixture of acetone and ether and dried under a vacuum.

Spectroelectrolysis grade acetonitrile (MCB) was degassed by freeze–pump–thaw cycles (<10$^{-5}$ torr). A MeCN/0.1 M TBAFP solution did not show appreciable Faradaic currents at a Pt electrode between -2.4 and +2.5 V vs. the Ag-wire quasi reference electrode (AgRE).

**Apparatus.** A Princeton Applied Research (PAR) Model 173 potentiosstat and a PAR Model 175 universal programmer were used for voltammetric experiments. The output of the PAR Model 176 current follower was recorded directly with a Houston Instruments Model 2000 X-Y recorder. The coulometric experiments employed a PAR 179 digital coulometer.

**Procedure.** The test solutions were prepared under He in a Vacuum Atmospheres glovebox equipped with a Model MO 40-1 Dri-Train. Electrochemical and ecl experiments were carried out in a three-compartment working cell with a volume of 3 cm$^3$. The working electrode compartment was provided with an optically flat Pyrex glass window of area approximately 2 cm$^2$, and the working electrode, a polished platinum disk of area 0.06 cm$^2$, was aligned parallel to the window. The distance between the working electrode and the window was about 3 mm. The counter electrode was a platinum foil, of area $\approx$3 cm$^2$. A silver wire immersed in the MeCN/TBAFP solution and separated from the working electrode chamber by a medium-porosity frit was used as a quasi reference electrode (AgRE). The potential of this Ag-wire electrode was measured against an aqueous calomel electrode (SCE) and checked vs. the ferrocene/ferrocenium couple in MeCN and was found to have a potential of +0.055 V vs. SCE.

The ecl measurements were carried out after transferring the sealed working cell to a light-tight box whose interior was painted with black nonreflective paint. The emitted light was measured with a Hamamatsu TV Corp. R928 photomultiplier tube. The ecl spectrum was taken using an Orilco Co. monochromator. Emission and absorption spectra were obtained with an Amino-Bowman spectrophotofluorometer (SPF) without slits for ecl studies and a Cary Model 14 UV and visible spectrophotometer, respectively.

Results and Discussion

**Electrochemical Results.** A typical cyclic voltammogram (CV) for 1 mM Ru(bpz)$_2$$^{2+}$ in MeCN/0.1 M TBAFP is shown in Figure 1. The peak potentials for the oxidation ($E_{pO}$) and reduction ($E_{pR}$) waves and $\Delta E_p$ values for each wave are given in Table I. The general electrochemical behavior of the Ru(bpz)$_2$$^{2+}$ system is very similar to that of Ru(bpy)$_3$$^{2+}$ in MeCN, but there are significant differences. The reductions to the 1+, 0, and 1– species and the oxidation to the 3+ species occur with all peaks shifted 0.5 V toward more positive potentials as compared to those for the bpy complex. Thus the Ru(bpz)$_2$$^{2+}$ species is a significantly stronger oxidant than is Ru(bpy)$_3$$^{2+}$, and its production from the 2+ form occurs much nearer to the anodic limit of the MeCN/TBAFP solution. Because of this, Ru(bpz)$_2$$^{2+}$ is less stable than the bpy complex in this medium, which leads to differences in the characteristics of the 3+/2+ wave and the ecl. On the other hand, the fourth reduction wave (marked V in Figure 1) shows a well-defined reversal peak at a scan rate, $\nu$, of 100 mV/s at room temperature, indicating some stability of the 2– species. No such stability is observed with the corresponding bpy form that is produced at a potential about 0.5 V more negative. Only at

![Figure 1. Cyclic voltammogram of 1 mM Ru(bpz)$_2$$^{2+}$(PF$_6$)$_2$/MeCN/0.1 M TBAFP at a Pt electrode (scan rate 100 mV/s, T = 25 °C, Ag-wire reference electrode).](image)

Table I. Cyclic Voltammetric Peak Potentials ($E_p$) for Ru(bpz)$_2$$^{2+}$ in 0.1 M TBAFP/Acetonitrile Solutions at a Platinum Electrode ($T = 25 ^\circ C$)

<table>
<thead>
<tr>
<th>Peaks in Figure 1</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{pO}(redn)$</td>
<td>+1.85</td>
<td>-0.800</td>
<td>-0.980</td>
<td>-1.250</td>
<td>-2.075</td>
</tr>
<tr>
<td>$E_{pR}(oxd.)$</td>
<td>+1.94</td>
<td>-0.730</td>
<td>-0.910</td>
<td>-1.180</td>
<td>-1.975</td>
</tr>
<tr>
<td>$\Delta E_p$ (25 °C)</td>
<td>90</td>
<td>70</td>
<td>70</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>100 mV/s, V</td>
<td>3+/2+</td>
<td>2+/1+</td>
<td>1+</td>
<td>0/-</td>
<td>1+/2-</td>
</tr>
</tbody>
</table>

* Potential values were measured against an Ag-wire quasi reference electrode in the same solution. The Ag wire showed a potential of +55 mV measured against a SCE in the same solution.

$v > 20$ V/s or at temperatures of $-30$ °C was any reversal anodic peak seen for the corresponding bpy wave. However, repeated scanning over wave V to produce the reduced 2– form led to the formation of a deep brown solution caused by decomposition of this species. Moreover, the rest potential of this solution after this cycling was --0.2 V vs. AgRE as compared to the initial value of about +0.54 V, indicating irreversible production of a reduced species. The resulting brown solution could not be electrochemically oxidized back to the original orange Ru(bpz)$_2$$^{2+}$ solution. Similar, but slower, decomposition occurred upon scanning or holding the potential at values corresponding to peaks III and IV (Figure 1).

The one-electron nature of the waves was confirmed by controlled-potential coulometry (CPC) measurements. Reduction at --0.8 vs. AgRE near the peak of the first reduction wave (wave, II, Figure 1) gave an $n_{app}$ value (corresponding to the number of faradays per mole) of 0.98. Oxidation of the reduced solution back to the 2+ form showed $Q_b/Q_f \approx 0.9$ (where $Q_b$ and $Q_f$ are the number of coulombs consumed during the forward reduction and reverse oxidation, respectively) for an experimental duration of $\approx 1$ h. This demonstrates the relatively high stability of the 1+ species.

Cyclic voltammetric data for the reduction waves (II–IV) shown in Figure 1 are contained in Table II. Because of the close spacing of the reduction waves, it was difficult to determine precise values for peak currents ($i_{pO}$ and $i_{pR}$) and potentials. However, the current functions ($i_{pO}/i_{pR}$) for all three waves are about the same, demonstrating that all three are one-electron transfers. Moreover, the values of $i_{pO}/i_{pR}$ $\approx 1$ for these waves demonstrate that the 1+, 0, and 1– forms are stable on the CV time scale.

(6) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980: (a) p 479; (b) p 455.
Table II. Cyclic Voltammetric Results for the Three Reductions of Ru(bpz)$_2^{2+}$

<table>
<thead>
<tr>
<th></th>
<th>peak II</th>
<th>peak III</th>
<th>peak IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$, mV/sec</td>
<td>$\Delta E_p$, mV</td>
<td>$i_{pa}/i_{pc}$</td>
<td>$i_{pa}/i_{pc}/\nu^{1/2}$</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>1.0</td>
<td>1.2</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>1.40</td>
<td>1.0</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>1.11</td>
<td>0.9</td>
</tr>
<tr>
<td>200</td>
<td>70</td>
<td>1.45</td>
<td>0.6</td>
</tr>
<tr>
<td>500</td>
<td>90</td>
<td>1.28</td>
<td>0.6</td>
</tr>
<tr>
<td>1000</td>
<td>100</td>
<td>1.45</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The solution was 1.0 mM Ru(bpz)$_2^{2+}$ (PF$_6$)$_2$ and 0.1 M TBAFP in CH$_2$CN at 25 °C. $\Delta E_p = E_{pc} - E_{pa}$, $C$ = concentration of complex. 

Figure 2. Ratio between the anodic and cathodic charges in wave I as a function of the scan rate ($T = 25 ^\circ C$). The solution is the same as in Figure 1.

For wave II the value of $i_{pa}/i_{pc}$ is significantly larger than 1; this suggests that some deposition or adsorption of the 1+ species occurs on the electrode. Although the CV data show stability of the 0 and 1- forms on the short time scale, repeated cycling through these waves causes some color change in the solution as well as the formation of a deposit on the electrode surface.

As for wave I, corresponding to the 3+/2+ oxidation-reduction process, the potential for this wave is close to the anodic stability limit of Pt in MeCN and the Ru(bpz)$_2^{2+}$ species reacts with a component in the MeCN/TBAFP medium to regenerate the 2+ species, giving rise to a catalytic wave. The CV parameters for wave I confirm the catalytic nature of this wave. For example, as shown in Figure 2, the ratio of peak heights, $i_{pa}/i_{pc}$ or peak areas, $Q_p/Q_o$, increases sharply with decreasing $v$. At low scan rates the ratio $Q_p/Q_o$ is very high since the 2+ species is continuously regenerated during the scan. At higher scan rates the ratio approaches unity because no appreciable reaction of the 3+ form occurs at short times.

A voltammogram taken after repeated application of pulses between -0.8 and +1.9 V vs. AgRE (the range for ecl, as described below), as shown in Figure 3, suggests decomposition of the Ru(bpz)$_2^{2+}$ complex since new peaks at +1.5 V vs. AgRE near wave I and at -0.4 vs. AgRE before wave II appear. The new anodic peak at +1.5 V appears after a cathodic scan to +1.2 V, and the new cathodic peak at -0.4 appears after a scan to +2.2 V. The species giving rise to these waves is not known.

After repeated pulsing experiments, the electrode surface was covered with a yellow-brown precipitate. Although the nature of this precipitate was not elucidated, it probably can be attributed to the formation of reduced Ru species. The decomposition process is enhanced when the cathodic scan limit is more negative.

Figure 3. Cyclic voltammogram of 1 mM Ru(bpz)$_2^{2+}$(PF$_6$)$_2$/MeCN/0.1 M TBAFP after repeated pulsing between -0.8 and +1.9 V vs. AgRE.

Figure 4. Luminescence spectrum of a 10$^{-5}$ M solution of Ru(bpz)$_2^{2+}$ in MeCN at room temperature.

Figure 5. Ecl spectrum of a 1 mM Ru(bpz)$_2^{2+}$(PF$_6$)$_2$/MeCN/0.1 M TBAFP solution (pulsing limits -0.8 and +1.85 V vs. AgRE at 0.5 Hz).

Emission Spectrum of Ru(bpz)$_2^{2+}$. The emission spectrum of a 10$^{-5}$ M solution of Ru(bpz)$_2^{2+}$ in MeCN at room temperature is shown in Figure 4. An excitation wavelength for maximum absorption (435 nm) leads to the emission maximum at 585 nm for the luminescence of the sample. This wavelength is 25 nm shorter than the emission maximum of Ru(bpy)$_3^{2+}$.

Ecl spectrum of Ru(bpz)$_2^{2+}$ in Acetonitrile. By pulsing of the potential applied to the platinum electrode between 1.95 and -0.85 V vs. AgRE an orange ecl emission was observed. The light intensity obtained was lower than that for Ru(bpy)$_3^{2+}$ under equivalent conditions and decayed more rapidly. The ecl spectrum of Ru(bpz)$_2^{2+}$ (Figure 5) shows an emission maximum at 585 nm, identical with the emission spectrum obtained on photoexcitation. These results are similar to those obtained with Ru(bpy)$_3^{2+}$. The mechanism for emission is
probably the same in both cases, namely, reaction of the 3+ and 1+ forms to yield the 2+ excited state (eq 1–3). This

\[
\text{Ru(bpz)}_3^{2+} + e^- \rightarrow \text{Ru(bpz)}_3^{3+}
\]  
(1)

\[
\text{Ru(bpz)}_3^{2+} - \text{e}^- \rightarrow \text{Ru(bpz)}_3^{3+}
\]  
(2)

\[
\text{Ru(bpz)}_3^{3+} + \text{Ru(bpz)}_3^{2+} \rightarrow \text{Ru(bpz)}_3^{3+} + \text{Ru(bpz)}_3^{2+}
\]  
(3)

homogeneous redox reaction has a free energy of −2.7 eV (as calculated from the \(E_v\) values of the 3+ / 2+ and 2+ / 1+ and waves, with the assumption of an entropic contribution of 0.1 eV). This is greater than the energy of the emitting charge-transfer state, 2.12 eV. The singlet excited state for \(\text{Ru(bpz)}_3^{2+}\) occurs at 2.85 eV \(\pm 0.1\) so that direct population of this state does not appear possible, and direct formation of the emitting triplet is proposed. This is analogous to the results in the \(\text{Ru(bpz)}_3^{3+}\) system.24

**Characteristics of the Ecl.** Recent studies26,3 of the ecl intensity \((I/I_0)^{1/2}\) behavior (where \(I_0\) is the forward pulse time and \(I\) the reverse pulse time) for the \(\text{Ru(bpz)}_3^{2+}\) system at short times \((I/I_0)^{1/2} = 1–10\) showed that these Feldberg-Faulkner plots8,10 corresponded closely to that expected of an “S-route” system, where direct population of the emitting state on electron transfer occurs. Similar plots for the \(\text{Ru(bpz)}_3^{2+}\) system are shown in Figure 6. When either the 1+ (Figure 6a) or the 3+ (Figure 6b) form is generated first, the behavior is very different from that of the theoretical model, which predicts a slope of −1.42. The cause for this deviation is probably the instability of the 3+ form and perhaps quenching by decomposition products. This nonideal behavior is also apparent from the ecl intensity–time transient itself (Figure 7). The anodic transient (following production of the 1+ species) shows a peak that decays to an almost steady value. This attainment of a steady value is also apparent from the change in slope in the plot of Figure 6a. The following cathodic transient is very sharp and decays rapidly to background. The steady level of emission during the anodic pulse represents a reaction of the 3+ species with solvent, electrolyte, or impurities to produce emission. That this is clearly the case can be seen from the anodic transient in Figure 8, where the potential was maintained at +1.90 V and a constant weak emission was observed. Recent studies have shown that the reaction of \(\text{Ru(bpz)}_3^{2+}\) with oxalate, organic acids, or other reductants results in emission,4,6,11,12 so a similar reaction by the stronger oxidant \(\text{Ru(bpz)}_3^{3+}\) appears reasonable. Thus the anodic step involves the 1+ / 3+ electron-transfer reaction as well as the 3+ / background emission. During the subsequent cathodic step the 3+ species has been depleted by this background reaction and less is available to react with the generated 1+ species, producing the rapid decay of intensity.

**Conclusions.** The electrochemical behavior of the \(\text{Ru(bpz)}_3^{2+}\) system generally parallels that of the corresponding bpy system, but the peaks are shifted by about 0.5 V toward more positive potentials. Since the 2+ / 3+ wave is best represented by electron transfers involving metal centers, the shift must be ascribed to greater stabilization of the 2+ vs. the 3+ form by bpy. The reduction waves, e.g., the 2+ / 1+ wave, are better represented as reduction of the ligands, and the shift here represents easier reduction of bpy to the \(\text{Ru}^{2+}\) stabilized bpy-

\[
\text{Ru(bpz)}_3^{2+} \rightarrow \text{Ru(bpz)}_3^{3+} + \text{Ru(bpz)}_3^{2+}
\]

and \(\text{Ru(bpz)}_3^{3+}\) species compared to that for bpy. The positive potential shift results in the 3+ bpy species being less stable in MeCN than the corresponding bpy species. Ecl reactions involving the 3+/1+ electron-transfer annihilation reaction and a reaction of the 3+ species with solvent or impurity to produce the \(\text{Ru(bpz)}_3^{2+}\) excited states occur. There is precedence for both of these in the bpy system.

**Acknowledgment.** The support of this research by the Office of Naval Research (Grant No. N00014-78-C-0592) and the Army Research Office (Grant No. DAAG 29-82-K-0006) is gratefully acknowledged. J.G.-V. is grateful to the Comité Hispano-Norteamericano de Cooperacion Cientifica y Tecnica for a grant.

**Registry No.** \(\text{Ru(bpz)}_3^{2+}\) (PF₆)₃, 80907-56-8; \(\text{Ru(bpz)}_3^{3+}\), 84303-43-5; \(\text{Ru(bpz)}_3^{2+}\), 75523-97-6; \(\text{Ru(bpz)}_3^{3+}\), 75523-95-4; \(\text{Ru(bpz)}_3^{2+}\), 75523-94-3; \(\text{Ru(bpz)}_3^{2+}\), 84303-44-6.