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Abstract
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TEMPERATURE AND SOLVENT-DEPENDENT LUMINESCENT PROPERTIES OF TRIS(2,2'-BIFURIDYL)RUTHENIUM (II) CHLORIDE

By

William R. Collin

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Senior Honors Thesis

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Abstract: Experimental studies on the luminescent properties of ruthenium based complexes have shown an excited state lifetime dependence on the solvent and temperature. An activation energy for the metal to ligand charge transfer (MLCT) based luminescence decay properties of tris(2,2'-bipyridine)ruthenium(II) chloride has been determined in various solvents. The results indicate a solvent influence on this decay. A model is being developed to correlate the lifetimes with interactions of the chromophore with the solvent to aid in the development of future sensors.

Introduction: Ruthenium ligand interactions in solvent systems have been studied for at least three decades.¹ A ligand is defined as a group, ion, or molecule coordinated to a central atom in a complex². A complex is further defined as a composite of chemical or immunological structures². This thesis will explore two main topics. The first part of this paper will focus on general behavior of ruthenium-ligand interactions. The second portion of the paper will focus on the behavior of a specific ruthenium-ligand complex under various experimental conditions.

To understand the photophysical behavior of the system, a discussion about excitation and relaxation of the molecular states will be useful. The molecule is first energized by a high energy pulse of green light from a laser. When this high energy light interacts with the outer electrons of the ruthenium-ligand complex, electrons are excited from the ground state to an excited state. The ground state of a molecule is defined as the lowest possible energy that a molecule can have. Molecules are most stable when they are at their lowest energy state. When additional energy is added to the system, like that
from a high intensity laser light through a solution of the complex, the molecule can be “excited” into one of several excited singlet states, as shown in the Figure 1.

**Figure 1:** The excited states of a molecule

The relevant states in this experiment are the first singlet and the first triplet states. The ground state can then be attained from an excited state through several processes. Depending on which excited state the molecule is in, the second singlet state or the first singlet state, the molecule will lose energy until it is in the lowest vibrational state of the lowest energy singlet state. Electronically excited molecules in the lowest singlet state then decay into their ground state through one of three processes: internal conversion, fluorescence, and intersystem crossing.

Decay within a given state is by relaxation from high vibrational states to lower vibrational states. This occurs by the emission of infrared light or by transfer of energy to
the solvent. Very often a high vibrational state of a lower energy electronic state will overlap with a low vibrational state of a higher electronic state molecule. Two states with equivalent energy are referred to as degenerate. A molecule can utilize this degeneracy to relax from a high electronic-low vibrational state to a low electronic-high vibration state.

Internal conversion is the process by which the lowest energy singlet state loses energy without radiation of light until it is in the ground state. This process takes place in microseconds or even picoseconds (a microsecond is 0.000001 seconds and a picosecond is 0.000000000001 seconds.) Without radiation and at such high speeds, this process is very difficult to measure. Fluorescence converts the excited state to the ground state through the emission of light. This is possible to measure, however it would require isolation of the fluorescence from the light of the laser, and a fast detection system because fluorescence occurs fast, typically on the timescale of picoseconds to nanoseconds. Also prohibiting the measurement of fluorescence is the time frame, again picoseconds to microseconds.

Intersystem crossing is the process by which the excited state decays from the singlet state to a triplet state. From the triplet state, the molecule can then phosphoresce, ultimately reaching the ground state. This is the easiest transition to measure because it takes place in microseconds or milliseconds, which is much easier to measure than the picoseconds associated with fluorescence. Due to the longer life of the decay, combined with the fact that the laser pulse is very short, this means that the phosphorescence lasts longer than the laser pulse, and allows for detection without laser interference. This is the process which was studied in this thesis. Measuring how long the phosphorescence gives valuable information about how the chemical system operates. Changing different parameters such as temperature, the solvent that the molecule is dissolved in, and what is
attached to the molecule, changes the lifetime. Varying the temperature is something that has not been done extensively before now, and the results from the work show a relationship between temperature and lifetime.

Work has shown that the metal ion concentration of the solution directly affects the lifetime of the excited state molecule by acting as a quenching agent. Quenching agents provide another non-radiative pathway for decay. If a lifetime versus concentration of metal plot is made, then unknown samples can be measured and metal concentrations can then be determined in the unknown solution. This method is very sensitive to iron, measuring concentrations as low 0.5 mM.

Interference to the iron determination comes from oxygen. If the system is free from metal ions, oxygen in the system shortens the lifetime. Using fluorinated xerogels in conjunction with tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium(II) chloride pentahydrate, Bukowski, Ciriminna, Pagliaro, and Bright developed an application of this principle to develop an oxygen sensor with sensitive detection and fast response times.

Perhaps the most interesting application of ruthenium-ligand complexes is their possible use to harness the energy of sunlight to split water into molecular oxygen and hydrogen, as outlined in the synthetic process below, Figure 2. This hydrogen and oxygen can then be recombined to produce energy. This method enables the production of hydrogen and oxygen without the need for storage, which is safer than the alternative.

\[
\text{RuL}_3^{2+} + \text{hv(light)} \rightarrow \text{*RuL}_3^{2+} \text{(excited)} \\
\text{*RuL}_3^{2+} + \text{Q(oxidant)} \rightarrow \text{RuL}_3^{3+} + \text{Q}^- \\
\text{2RuL}_3^{3+} + \text{H}_2\text{O} \rightarrow \text{2RuL}_3^{2+} + \frac{1}{2} \text{O}_2 + \text{2H}^+ \\
\text{Q}^- + \text{H}^+ \rightarrow \text{Q} + \frac{1}{2} \text{H}_2
\]

**Figure 2:** Synthesis of hydrogen and oxygen from water.
In this process, an excited ruthenium-ligand complex is oxidized by some oxidant Q. The oxidized form of the complex then oxidizes water to form molecular oxygen and hydrogen ions, forming the first product oxygen and regenerating a relaxed complex that can be excited again. The oxidant in its reduced form is oxidized by hydrogen ion to form hydrogen gas, returning the oxidant to its oxidizing form. The only reactants consumed in the reaction are water and light; all other species are regenerated and able to be used in the cycle again. Thus with adequate water supply and light, hydrogen and oxygen gases can be produced for combustion to create energy. The only problem with this system is keeping the initial excited ruthenium-ligand complex around long enough to react in the second step. This gets to the heart of this research project, extending the lifetime of the excited state so that it can be used to do the above reaction series.

**Experimental:** A schematic diagram of the experimental setup is shown in Figure 3. Each component will be discussed separately for ease of understanding of how the system works.

![Figure 3: Schematic diagram of measurement system](image)
A) Laser (Figure 4)

The laser is a Nd:YAG pulsed laser made by New Wave Research, operating at 532 nm. The system emits a ten nanosecond laser pulse every ten times a second, which is sufficient time to record the decay before the next pulse initiates another absorption event. The laser has a pulse width of a nanosecond in order to detect phosphorescence which occurs on the micro to millisecond time scale. The high rate of measurement allows for a high number of individual decay spectra to be averaged, increasing the signal.
to noise ratio. The reason for using a high intensity source is to insure enough molecules are excited to make an accurate measure of the general properties of the system. Ambient light does not excite enough atoms to produce measurable phosphorescence, making a laser necessary for the measurements required by the experiment.

![Figure 5: Sample Cell and temperature controlling cell holder used in the experiment.](image)

**B) Sample Cell, Deoxygenation System, and Temperature Controller (Figure 5)**

The sample cell used in this experiment is a 1cm glass cuvette. The solution is deoxygenated by a custom made stopper with three hypodermic wires protruding through. The wires are attached to a larger tube which is in turn attached to a needle valve on a nitrogen gas cylinder. This allows a constant stream of nitrogen bubbles to be sent through the sample, removing oxygen from the solution with it. A Fisher Scientific Isotemp Model 900 temperature controller was used in the range from -30°C to 60°C. The
low temperatures were accomplished by replacing the solution in the system with a 1:1 ratio of ethylene glycol to water.

Figure 6: The detector used in the experiment.

C) Detector and Oscilloscope/PC (Figure 6)

The detector for the phosphorescence is a Hamamatsu photomultiplier tube. Special care was taken to insure that no stray light, or reflected laser light, interfered with accurate measurement of the weak phosphorescent light. For each test run, 64 decay spectra, each containing at least 1000 data points, were averaged on an HP-54615B oscilloscope. The oscilloscope data was fed into an HP Brio PC via GPIB input and BenchLink software. The resultant graphs were analyzed with Origin 6.1. Exponential
decay constants were determined for each graph, giving the lifetime of the first triplet state.

**Sample Preparation**

Since the ruthenium tris(bpy) complex is very sensitive to light, the stock solid was kept in an amber container which was then wrapped in aluminum foil to keep light out. Another precaution taken to avoid error due to decay was making solutions on a weekly basis. Very small concentrations are necessary for this experiment as high concentration leads dimer formation which leads to erroneous data. Therefore, serial dilutions were done to accurately get low concentration solutions. Regardless of the solvent used, the solutions were made to be 10 µM in tris(bipyridyl) ruthenium (II) chloride. Solvents used were methanol, 0.1M HCl, 1,2-propanediol, and glycerol.

**Lifetime Decay**

Each sample was placed in the cuvette using a Pasteur pipette. The cell was then placed in the temperature controlled platform. The nitrogen bubbler was then placed in the cell, and allowed to deoxygenate the system for at least five minutes. There was no change in lifetime within error if the deoxygenation system was used for longer periods of time. The solutions of glycerol were not deoxygenated due to the high viscosity of the solvent. Any bubbles in the system did not rise to the top and break; they simply stayed in the solution. This is an undesirable state since these bubbles reflect a lot of the laser light.

After deoxygenation and temperature adjustments, the sample was ready to be irradiated with the laser. When the system had enough time to average 64 spectra, the averaged data was captured by the computer and saved for analysis. A baseline spectrum was taken by turning the laser off and recording the signal.

**Analysis**
The data was analyzed by first subtracting the baseline from the actual data set. Figure 7 shows a typical curve after this step. Note the superfluous data in the initial excitation stage. This is from the laser overwhelming the phosphorescence in the excitation before it pulses off. This must be removed before any regression can be performed on the graph. This is accomplished by subtracting the baseline spectrum. The result of this step is shown in Figure 8.

**Figure 7: Decay of ruthenium complex in water**

**Figure 8: Decay of ruthenium complex in water**
At this point, a first order exponential decay curve was fit to the graph, as shown in Figure 9. The value of the constant $\tau$ gives the lifetime of the excited state as given in equation 1 below:

$$I = Ae^{-t/\tau} \quad (1)$$

Where $I$ is the intensity of the response, and $A$ is a constant.

This process is typical of the experimental method and was followed for all temperatures and solvent systems unless otherwise noted.

Results:

Solutions of ruthenium (II) tris(bipyridyl)chloride in 0.1 M HCl served as the basis for comparison of all solvents due to the extensive body of research already done on this system. Aqueous analyses in this experiment included quenching effects of Fe$^{3+}$, temperature variation, and deoxygenation and combinations of all three.

From the lifetime’s temperature dependence, it is possible to determine the energy level spacing between d-$\pi^*$ states and d-d transition states as shown in Figure 10 below.
The relationship between the lifetime of the excited state and the energy difference between the states is given, then, by Equation 2. In Equation 2, \( \tau \) is the lifetime, \( T \) is the temperature, \( \Delta E \) is the energy level separation, \( k \) is Boltzman’s constant, \( k_{1r}, k_{1q}, \) and \( k_{2q} \) are non-radiative, fluorescence and phosphorescence constants respectively. Manipulation of this equation allows for the calculation of the energy difference from lifetime and temperature data. As it turns out, a plot of the natural log of the inverse of the lifetime against the inverse of the temperature will give a slope of \(-\Delta E/kT\) and from that the energy difference can be calculated. Figure 11 shows just such a lifetime vs. temperature relationship.

**Figure 10:** Relationship between transition states and temperature dependence of the states given by \( \tau_m(T) = [k_{1r} + k_{1q} + k_{2q}e^{-\Delta E/kT}]^{-1} \) (Eq 2)

**Figure 11:** Acid solution showing lifetime-temperature dependence
The presence of iron (III) ions in solution gave a decreased lifetime. This should have very little effect on the separation of the two states. In an attempt to prove this the temperature of a solution containing iron (III) ions was also tested at various temperatures. The result of this comparison is shown in Table 1 below.

Table 1: Energy level difference in unquenched and quenched aqueous solutions

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Slope of Plot</th>
<th>∆E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Free Acid</td>
<td>-1335.081</td>
<td>927.9 cm$^{-1}$</td>
</tr>
<tr>
<td>0.8 mM Iron Acid</td>
<td>-581.474</td>
<td>404.1 cm$^{-1}$</td>
</tr>
</tbody>
</table>

The unexpected difference of about 500 cm$^{-1}$ implies that the iron has a large effect on the separation of energy states. This is probably due to some sort of ligand-metal ion interaction. More work must be done to verify that there is such a large difference in the energy levels.

An even larger difference in energy levels can be obtained by changing solvents. Using methanol, instead of water as a solvent, gave even larger gaps in the energy levels, as shown in Table 2.

Table 2: Comparison of acid solution and methanol solution.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Slope of Plot</th>
<th>∆E</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M HCl</td>
<td>-1335.081</td>
<td>927.9 cm$^{-1}$</td>
</tr>
<tr>
<td>Methanol</td>
<td>-85.423</td>
<td>59.4 cm$^{-1}$</td>
</tr>
</tbody>
</table>

Comparing multiple solvents by calculating the lifetime of the excited state of tris(bipyridyl) ruthenium (II) chloride from the decay curves is useful to determine
which solvent system yields the longest lifetime. Figure 12 shows the solvent differences graphically and Table 3 shows tabulated values for the lifetimes.

![Multiple decay curves of tris(bipyridyl) ruthenium (II) chloride in multiple solutions](image)

**Figure 12: Multiple decay curves of tris(bipyridyl) ruthenium (II) chloride in multiple solutions**

**Table 3: Lifetime of excited state in various solvents.**

<table>
<thead>
<tr>
<th>Solvent Description</th>
<th>Lifetime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HCl Iron Quenched (0.8mM)</td>
<td>2.716 x 10^{-7}</td>
</tr>
<tr>
<td>0.1M HCl 1,2-Propanediol No deoxygenation</td>
<td>4.694 x 10^{-7}</td>
</tr>
<tr>
<td>1,2-Propanediol deoxygenated</td>
<td>8.565 x 10^{-7}</td>
</tr>
<tr>
<td>1,2-Propanediol Deoxygenation</td>
<td>1.105 x 10^{-6}</td>
</tr>
<tr>
<td>Methanol No Deoxygenation</td>
<td>2.524 x 10^{-7}</td>
</tr>
<tr>
<td>Methanol Deoxygenated</td>
<td>6.713 x 10^{-7}</td>
</tr>
<tr>
<td>Glycerol</td>
<td>5.390 x 10^{-7}</td>
</tr>
</tbody>
</table>

The longest lifetime of any solvent tested was 1,2-propanediol with deoxygenation. The effects of deoxygenation and quenching can also be seen in Table 3. Specifically, the largest effect on the lifetime seems to be from the 1,2-propanediol deoxygenated solvent.

An interesting venture into the effect of iron concentration on the system was investigated by varying the concentration of iron while holding all other variables constant and measuring the lifetime. Iron and oxygen have the effect of quenching the
excited state. The rate constant for the quenching effects can then be calculated based on Equation 3.

\[ \frac{1}{\tau'_p} = \text{constant} + k_q[\text{Fe}^{3+}] \]  

(Eq 3)

Where \( \tau_p \) is the lifetime without a quencher and \( \tau'_p \) is the lifetime with a quencher present. From the slope of a plot of \( \text{Fe}^{3+} \) concentration vs. lifetime, \( k_q \) is calculated. Figure 13 shows the plot, which gave a quenching constant of 1056 M\(^{-1}\)s\(^{-1}\).

![Plot showing best fit of quencher concentration vs. 1/lifetime](image)

**Figure 13: Plot showing best fit of quencher concentration vs. 1/lifetime**

To gain confidence in the data, a series of at least 10 lifetime measurements were made to see if individual values agreed with one another when all other variables are held
constant. Methanol and glycerol were used in this study, and the standard deviation of the data set was determined with Excel. The results show an error of less than 1 percent for methanol and less than 10 percent for glycerol. In either case, it was determined that any single measurement was close enough to the mean value for a given set of conditions that only one measurement needed to be taken for each set of conditions.

**Conclusion:** A number of interesting conclusions came out of this experiment. First, by varying the temperature of the solutions, calculating the separation between d-d transition states and d-π* transitions enables relatively easy comparison of different solvent systems. The combination of these two techniques, varying solvents and temperature, opens a new pathway to get information about the exited state lifetimes. The separation between the states gives a lot of information about the lifetime of the excited state; the larger the separation between states, the longer the lifetime. Therefore this method allows an investigator to compare results using a single number, thus streamlining the process of finding which conditions lengthen the lifetime.

Low temperature, highly viscous solvents show the longest lifetime as long as there is no oxygen present in the system. This implies that further research in this direction will be helpful in verifying and quantitating this effect. Adapting the current method at lower temperatures and using the deoxygenation in the highly viscous solvents might show further correlation between viscosity and lifetime. It was not practical to use deoxygenate the most viscous solvents, so a way to do this must be found before more data can be gathered along these lines.

Another direction this research could take in the future is that of changing the composition of the ligand attached to the ruthenium. For instance, comparing the structure of tris(bipyridyl) ruthenium (II) chloride and tris(phenanthroline) ruthenium (II)
there are two things that may prove interesting to investigate. The twist in the bipyridine structure hinders solvent access to the ruthenium, as compared to the phenanthroline structure in Figure 14.

![Molecular models of two ruthenium complexes.](image)

This should allow the excited state to relax without light emission, shortening the lifetime of the excited state. Competing with this effect is the poly-aromatic ring system with many open orbitals available for electrons to be shifted into, which should lengthen the lifetime of the excited state. Changing the ligand should allow for investigation of the effects of ring size and the effects of steric hindrance to the solvent on the lifetime of the excited state.

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