Tris(2,2'-bipyridine)ruthenium(II) Dichloride Hexahydrate

\[ \text{[Ru(bpy)}_3\text{]}\text{Cl}_2\cdot6\text{H}_2\text{O} \]
2,2'-Bipyridine

• 2,2'-bipyridine, commonly abbreviated as *bpy*, functions as a bidentate chelating ligand.

![2,2'-Bipyridine structure](image)

• The bpy in the phosphinic acid/ruthenium chloride solution complexes with the Ru$^{2+}$ produced by the redox reaction, and the complex is precipitated by adding excess Cl$^-$ (as KCl), using the common ion effect:

$$\text{Ru}^{2+} + 3\text{bpy} + 2\text{Cl}^- + 6\text{H}_2\text{O} \rightarrow [\text{Ru(bpy)}_3]\text{Cl}_2.6\text{H}_2\text{O}$$

• The [Ru(bpy)$_3$]$^{2+}$ in the product is actually a mixture of two optical isomers with $D_3$ symmetry.

![2,2'-Bipyridine optical isomers](image)
[Ru(bpy)$_3$]$^{2+}$ Electronic Structure

- Second-row transition ions, like Ru$^{2+}$ tend to have larger $\Delta_0$ values and smaller $P$ values.
- Also, bpy is a strong-field ligand, which tends to produce large $\Delta_0$ values.
- As a result, [Ru(bpy)$_3$]$^{2+}$ is a $d^6$ low-spin case, which is diamagnetic.
- [Ru(bpy)$_3$]$^{2+}$ has two bands at 428 nm and 454 nm with high extinction coefficients have been assigned to *metal-ligand charge-transfer* (MLCT)
- The absorption of the blue end of the spectrum gives the complex its characteristic red color.
- [Ru(bpy)$_3$]$^{2+}$ can be made to show *chemiluminescence*. 
Chemiluminescence

- *Chemiluminescence* is the production of visible light through a *chemically induced excited state* of a molecule, which relaxes back to the ground state by photon emission.

- *Fluorescence* is a short lifetime *photoluminescence* process (0.5-20 ns) in which a molecule emits a photon from a singlet excited state, thus quickly decaying back to its singlet ground state.

- Both the ground and excited states are singlet states \( (m = 2S + 1) \).

  \[ ^1M + h\nu \rightarrow ^1M^* \rightarrow ^1M + h\nu \]

- \(^1M^*\) can also lose energy by non-radiative processes (thermal motion, vibration, molecular quenching), resulting in no light emission, i.e. non-radiative decay.
• *Phosphorescence* is a longer lifetime *photoluminescence* process (µs - hours) in which the excited molecule undergoes an intersystem crossing (*isc*) to a triplet excited state.

• Radiative transition from an excited triplet state to the singlet ground state is quantum mechanically “forbidden” but occurs with low efficiency, resulting in longer lifetimes.

\[
{^1M + h\nu \rightarrow ^1M^* \rightarrow ^3M^* \rightarrow ^1M + h\nu'}
\]
Jablonski diagram

Potential energy

FC state
thexi state

S_n

S_1

S_0

T_n

T_1

hv

ic internal conversion
isc intersystem crossing
vr vibrational relaxation
fl fluorescence decay
ph phosphorescence decay
Procedure Notes

• Start by preparing the 10 % aqueous acetone solution needed for the first wash by chilling it on ice so that it will be ready when needed.

• A 31 % phosphinic acid solution has been prepared for use in making the NaH$_2$PO$_2$ solution.

• Converting 2 mL of the acid to a solution of the sodium salt should take about 6-7 NaOH pellets.

• Once the solution becomes slightly cloudy, add phosphinic acid dropwise until the precipitate just dissolves.

• We will not record a quantitative UV-Vis spectrum of [Ru(bpy)$_3$]$^{2+}$. Just make up a solution, take a qualitative spectrum, and adjust the concentration if needed to obtain a decent spectrum to be submitted with your report.

• For point 1 of the write-up, simply comment on the purity of the compound on the basis of the number and positions of the bands, compared to the data given in the experimental procedure.

• For the chemiluminescence experiment, adjusting the pH using a 2 M HCl solution (pH indicator paper) and observe the chemiluminescence in the dark.
Redox Chemistry

- Ruthenium is a second-row transition element, under iron in the periodic table.
  \[ \text{Ru}^0 (4d^65s^2) - 2e^- \rightarrow \text{Rn}^{2+} (4d^6) - e^- \rightarrow \text{Ru}^{3+} (4d^5) \]

- Ru\(^{3+}\) (aq) is a moderate oxidizing agent:
  \[ \text{Ru}^{3+} (aq) + e^- \rightarrow \text{Ru}^{2+} (aq) \quad E^o = +0.249 \text{ V} \]

- In this synthesis Ru\(^{3+}\) is reduced with phosphinic acid:
  \[ \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 2\text{H}^+ + 2e^- \quad E^o = +0.499 \text{ V} \]
  \[ \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2e^- \quad E^o = +0.276 \text{ V} \]

- This synthesis uses oven-dried RuCl\(_3\).xH\(_2\)O, which is reduced with freshly prepared NaH\(_2\)PO\(_2\), sodium phosphinate:
  \[ \text{H}_3\text{PO}_2(aq) + \text{NaOH}(aq) \rightarrow \text{NaH}_2\text{PO}_2(aq) + \text{H}_2\text{O} \]
  \[ \text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_4^- + 4\text{H}^+ + 4e^- \]
  \[ 4(\text{Ru}^{3+} + e^- \rightarrow \text{Ru}^{2+}) \]
  \[ \text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} + 4\text{Ru}^{3+} \rightarrow \text{H}_2\text{PO}_4^- + 4\text{H}^+ + 4\text{Ru}^{2+} \]
Chemiluminescence of $[\text{Ru(bpy)}_3]^{2+}$

- In this experiment, $[\text{Ru(bpy)}_3]^{2+}$ is mixed with the strong oxidant $S_2\text{O}_8^{2-}$ and both are reduced by reaction with Mg(s).

- The reduction product of $S_2\text{O}_8^{2-}$ is the highly reactive species $\text{SO}_4^{\cdot-}$ which oxidizes $[\text{Ru(bpy)}_3]^+$ back up to $[\text{Ru(bpy)}_3]^{2+}$ in an excited state.

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2e^-$$

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

$$S_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{\cdot-}$$

$$[\text{Ru(bpy)}_3]^+ + \text{SO}_4^{\cdot-} \rightarrow \{[\text{Ru(bpy)}_3]^{2+}\}^* + \text{SO}_4^{2-}$$

- The excited state species phosphoresces, emitting bright orange light at 610 nm:

$$\{[\text{Ru(bpy)}_3]^{2+}\}^* \rightarrow [\text{Ru(bpy)}_3]^{2+} + h\nu$$