

Tris-2,2'-bipyridine Complexes of Iron(II) and Ruthenium (II): Synthesis, Spectroscopy and Electrochemistry

Polypyridyl complexes of the type $[M(\text{bpy})_3]^{2+}$ have been studied intensively in part because of possible applications of their excited state properties to energy conversion processes. In this experiment the complexes $[\text{Fe}(\text{bpy})_3](\text{BF}_4)_2$ and $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$ will be synthesized. The absorption and emission spectra of each will be obtained and the results will be used to construct a qualitative molecular orbital depiction of the two molecules. Electrochemistry can be used to probe the electronic characteristics of redox-active transition metal complexes. In particular, you will investigate the frontier orbitals (HOMO and LUMO) of each complex *via* Cyclic Voltammetry.

Experimental:

Synthesis of $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$

Place 1 mmol (ca. 275 mg) of RuCl_3 in a 50 mL Erlenmeyer flask with 10 mL 1,5-pentanediol, 1 mL of H_2O and a stir bar. Heat and stir until the metal salt dissolves, then add 3.5 mmol of 2,2'-bipyridine ($\text{C}_{10}\text{H}_8\text{N}_2$) and 0.5-1.0 mmol ascorbic acid and heat to boiling for 15 min. Allow the reaction mixture to cool, dilute it to about 40 mL with H_2O , and adjust the pH of this solution to about 8 using dilute sodium hydroxide. If necessary, filter the solution to clarify it, then precipitate the product by adding an excess (~5g) of NaBF_4 . The orange solid recovered is $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$.

Synthesis of $[\text{Fe}(\text{bpy})_3](\text{BF}_4)_2$

FeCl_2 (0.1 g) is dissolved in a minimum amount of water and *bpy* (0.4 g) is dissolved in a minimum amount of ethanol. The two solutions are mixed and a solution of NaBF_4 (0.2 g) in water is added. The resulting deep red precipitate is filtered and washed with cold water and finally cold ethanol.

UV-Visible Spectra

Record the UV-visible spectra of the two complexes in acetonitrile (25-50 mL of solution) from 850 to 250 nm. Calculate the maximum molar absorptivity (ϵ_{max}) of each absorption band for the two compounds. (*Note*: It will be necessary to record spectra

over a range of concentrations in order to observe all transitions, as a first guess try 25 μM ($10^{-6} = \mu\text{M}$). What are the similarities and differences between the spectra of the two complexes? What electronic transition is responsible for the color of each complex? Is the color due to $d \rightarrow d$, metal \rightarrow ligand charge transfer (MLCT), or ligand \rightarrow metal charge transfer (LMCT) processes?

Fluorescence Spectra

Immediately prior to the emission measurements, transfer enough solution (use the same solution that was used for UV-vis measurements) to a 1 cm fluorescence cell purge the solution in the cell for 30-40 sec. And cap immediately. The excitation wavelength should be set to the absorption band of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$. The emission spectrum should be collected between 400-700 nm. Explain the differences observed between the two complexes.

Electrochemical Studies

You will probe the redox behavior of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$. Cyclic Voltammetry (CV) will be used to make the measurements. Make up 50 mL of acetonitrile/0.1 M TEABF₄ (tetraethylammonium tetrafluoroborate), set up the electrochemical cell and bubble the solution with argon or nitrogen for approx. 20 minutes. Why is it necessary to purge the solution of air prior to obtaining the CV? Check that the back ground solvent is free of redox processes by running positive and negative CV's. Add approx. 20 mg of the compound. Set the starting potential at 0 V and scan at a rate of 100 mV/sec, sweep to +2 V and -2V. How many oxidation and reduction processes are observed in each complex? Tabulate the $E_{1/2}$ for each electrochemical process in each complex. Convert the $E_{1/2}$ values to ΔG values ($\Delta G_{1/2} = -n\mathcal{F}E^0$) and the $E_{1/2}$ value of the reference electrode. Compare the energy gap between the first reduction process and the oxidation process with the energy of the visible absorption maximum of $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{bpy})_3]^{2+}$. Focus in on the reduction processes for each, obtain a decent voltammogram of the reduction processes for the two complexes. Record the oxidative voltammograms at a range of scan rates to determine if them processes are reversible. If a redox couple is fully reversible, then the following criteria must hold:

- a. E_p is independent of v (scan rate) and $E_a - E_c = 59/n$ mV (n = the number of electrons involved in the electron transfer process) at 298 K. and $E_p = (E_a + E_c)/2$ where E_a = the anodic peak potential and E_c = the cathodic peak potential.
- b. $i_a/i_c = 1.0$ and i_a vs. $v^{1/2}$ is a straight line through zero. i_a = anodic peak current, i_c = cathodic peak current.

Molecular Orbital Description

Construct a semi-quantitative molecular orbital diagram for the two complexes (*bpy* is a bidentate N-donor ligand and is a fairly good π -acceptor ligand) based on the spectroscopic and electrochemical data. Where are the HOMO and LUMO primarily based? What are the major differences between the MO descriptions for each complex? What is spin-orbit coupling? It has been found that the intensity of the MLCT transitions in $[M(\text{bpy})_3]^{2+}$ type complexes are proportional to λ^2 (λ is the spin-orbit coupling constant). Is the experimental data consistent with the expected trend in spin-orbit coupling? Does spin-orbit coupling help in explaining the observed differences between MO diagrams of $[\text{Fe}(\text{bpy})_3](\text{BF}_4)_2$ and $[\text{Ru}(\text{bpy})_3](\text{BF}_4)_2$?

Potentially Useful References:

Demus, J. N.; DeGraff, B. A. *Analytical Chemistry* **1991**, *63*, 829 A.
Kober, E. M.; Meyer, T. J. *Inorganic Chemistry* 1982, *21*, 3967.