Synthesis and Electrochemical Properties of $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5$: A Light Absorber – Electron Collector – Light Absorber Triad

AND

Development and Evaluation of Integrated Molecular Modeling, Synthesis, and Characterization Laboratory Experiments for the Undergraduate Chemistry Curriculum

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(Abstract)

The research detailed herein has been conducted in two different areas. The first research goal was to develop and study a supramolecular system coupling two light absorber units to a central metal site capable of collecting two electrons; this has been accomplished.

The complex $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5$ was synthesized and characterized using electrochemistry and electronic absorption spectroscopy. The electrochemical properties of $\{[(bpy)_2Ru(dpp)]_2RhCl_2\}(PF_6)_5$ were probed with cyclic voltammetry and bulk electrolysis studies to investigate the behavior of the system upon two-electron reduction of the rhodium metal center. Bulk electrolysis showed that the rhodium center underwent two-electron reduction. A water modulation of product distribution for the bulk electrolysis studies was found, and the nature of this process was studied. In the presence of water, two-electron reduction of the rhodium metal center afforded a Rh^I complex that had lost two chloride ligands: $\{[(bpy)_2Ru(dpp)]_2Rh^I\}^{+5}$. In the absence of

sufficient water, two-electron reduction yields a breakdown of the trimetallic resulting in $[(bpy)_2Ru(dpp)]^{+2}$ and $\{[(bpy)_2Ru(dpp)]Rh^{I}Cl_2\}^{+}$.

The second research goal was to develop integrated molecular modeling, synthesis, and characterization laboratory experiments, to incorporate into the undergraduate inorganic laboratory curriculum, and to evaluate and modify this curricular approach. This was accomplished with organometallic $[Mo(CO)_4(N\text{-}N)]$ complexes, where N-N is a bidentate nitrogen donor ligand. $[Mo(CO)_4(N\text{-}N)]$ complexes were selected because they were amendable to molecular modeling and could be synthesized via two synthetic routes with reasonable yields, low reaction times, and were air stable.

Many of these complexes are new, so a series of $[Mo(CO)_4(N\text{-}N)]$ complexes were synthesized by either thermal or photochemical substitution reactions. The systems were characterized using cyclic voltammetry, electronic absorption spectroscopy, and ^1H NMR spectroscopy.

Molecular modeling was performed on the series of $[Mo(CO)_4(N\text{-}N)]$ complexes using the CAChe software from Oxford Molecular, Ltd. These calculations typically provided reasonable structures, orbital locations, and relative orbital energies for the $[Mo(CO)_4(N\text{-}N)]$ systems.

Correlations between the computational and experimental data were established. The electronic absorption spectral MLCT frequency versus calculated HOMO-LUMO energy gap, E_p^a versus calculated HOMO energy, $E_{1/2}^{red}$ versus calculated LUMO energy, and ^1H NMR chemical shift for $[Mo(CO)_4(1,10\text{-phen})]$ and the substituted $[Mo(CO)_4(1,10\text{-phen})]$ complexes versus ZINDO calculated partial charge were compared, where 1,10-phen = 1,10-phenanthroline. From the analyses of physical versus computational data, it was concluded that molecular modeling results are useful in predicting physical data for these complexes.

The integrated molecular modeling, synthesis, and characterization experiment was developed and incorporated into the undergraduate inorganic chemistry laboratory. In both 1998 and 1999, a qualitative evaluation of student response was completed. This was done using a recorded interview technique; interviews were subsequently transcribed and rendered to extract themes. This interview style was an effective evaluation

technique for this project, providing the detailed comments and student feedback that were desired. These interviews showed that the majority of the students both enjoyed this experiment and felt that the exposure to molecular modeling was worthwhile within this type of integrated lab forum. The students felt this experiment aided in their understanding of the orbital properties of inorganic systems. Student comments and suggestions facilitated modifications for future offerings in 1999 and 2000. Continued evaluation and expansion of this curricular approach are in progress.