Chapter 12. Integrated Molecular Modeling, Synthesis, and Characterization Experiments for the Undergraduate Inorganic Chemistry Laboratory. Conclusions and Future Work

An integrated molecular modeling, synthesis, and characterization experiment has been developed and incorporated into the undergraduate inorganic chemistry laboratory curriculum. $[Mo(CO)_4(N\text{-}N)]$ complexes were selected for this study, because they can be synthesized via two synthetic routes with reasonable yields, low reaction times, and are air stable. Additionally, the body of $[Mo(CO)_4(N\text{-}N)]$ systems published in the literature is small, thus give students the opportunity to synthesize new complexes in the course. This experiment has been performed in the inorganic laboratory for the last three years. Student response to the integrated molecular modeling, synthesis, and characterization project has been evaluated using a qualitative interview approach. Student comments and suggestions for improvement have been incorporated into subsequent offerings.

For the purpose of experimental design, a small series of $[Mo(CO)_4(N\text{-}N)]$ complexes were modeled, and geometry optimization (MM1 or MM2), molecular orbitals (Extended Huckel and ZINDO/INDO 1), electron density (Extended Huckel and ZINDO/INDO 1), and calculated UV-visible spectra (ZINDO with CI) calculations were performed. These calculations provided structures and energies for the $[Mo(CO)_4(N\text{-}N)]$ complexes.

Correlations were tested between the experimental and computational data. The electronic absorption spectral MLCT energy versus calculated HOMO-LUMO gap, $E_p^{a\ oxd}$ and $E_{1/2}^{red}$ versus calculated HOMO and LUMO energies, and ZINDO calculated partial charge versus ^1H NMR chemical shift for $[Mo(CO)_4(1,10\text{-phen})]$ and the substituted $[Mo(CO)_4(1,10\text{-phen})]$ complexes at the 3, 6, and 8 hydrogen positions were compared. From the analyses of physical versus computational data, we concluded that molecular modeling results are useful in predicting physical data for these complexes, at least in a qualitative way. The student experiment involves the prediction of the physical properties of two $[Mo(CO)_4(N\text{-}N)]$ systems relative to each other. Our study of a small

series of complexes led us to believe that the qualitative prediction would be valid most of the time.

In both 1998 and 1999, a qualitative evaluation of student response was completed, using a recorded interview technique. This interview style was an effective evaluation technique for this project, providing the detailed comments and student feedback that were desired. Our evaluation techniques were especially useful in allowing for improvements in curricular design. From these interviews, we concluded that the majority of the students both enjoyed this experiment and felt that the exposure to molecular modeling was worthwhile. This exposure aided in their understanding of the orbital properties of inorganic systems. The CAChe molecular modeling software was well received, as were the varied synthetic approaches. Students suggested additional introductory materials, and more information on how modeling results are correlated to characterizational data. Student comments and suggestions have been addressed, and have aided in making modifications for future offerings.

The question still remains, is this good or bad for our experimental design? One of the underlying goals of this experiment was to show the students both the value and limitations of the use of modeling in research. Although reasonable qualitative relationships can be drawn between experimental and computational data for a series of complexes, when two such complexes are compared, the correlations are less effective. This is consistent with our experimental design, in that some relationships are effective and some are not, depending on both the properties measured and the complexes investigated. Thus, students are exposed to both the capabilities and limitations of molecular modeling technology.

Future Work.

Additional experiments for use in the inorganic laboratory are currently under development. In the first developmental experiment, free N-N ligands and the corresponding [$Mo(CO)_4$(N-N)] complexes are investigated, and predictions are made as to the physical properties of the N-N ligand upon binding to the metal. The second developmental experiment investigates the analogous [$Mo(CO)_4$(P-P)] complexes, where

P-P = a bidentate phosphine donor ligand. The use of phosphine ligands will require a more rigorous inert atmosphere techniques and introduce ^{31}P NMR spectroscopic characterization.

The general curricular design used in these experiments is quite adaptive, and it could be used in many other classroom/laboratory settings. The introduction of integrated modeling techniques may aid students in understanding structural physical or organic chemistry topics which are not easily grasped, for example, lowest energy configurations or isomerization.

Our evaluation techniques could easily be applied to other types of curricular approaches. This style of evaluation gives detailed student feedback, much more so than the classic "evaluation form"; thus specific comments and student suggestions about course content, techniques used, etc. may be taken into account when preparing for subsequent offerings. This is especially useful in upper level courses, where the class size is small enough that a thorough interview evaluation may be performed.