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COORDINATION CHEMISTRY REVIEWS

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Preface

One of the most important aspects of theoretical calculations in chemistry is not simply to reproduce numerical values of energies associated with chemical reactions, nor to reproduce the electronic or molecular structures of chemical compounds. Rather, calculations should ideally provide an insight into the factors involved in controlling chemical reactions. From these insights one should then be able to construct new theories and extract general principles that can act as guides in the many endeavors where our present interest, Coordination Chemistry (CC), is playing an important role. Such areas where CC is currently being productive range from the role of metal ions in biology to design of ligands for selective extraction of metal ions, or complexation of metal ions to act as imaging agents in diagnostic medicine. Molecular Mechanics (MM) is particularly suited as a tool for the analysis of steric effects, and has led to many insights in CC as described in the reviews presented in this volume. MM enjoys a particular advantage over semi-empirical wave-mechanical based calculations in modeling coordination compounds at the present time because, in the experience of the present author, semi-empirical calculations are rather unsuccessful at predicting the structure of even simple well-known coordination complexes. For example, the present author has not yet found a semi-empirical approach that will even correctly predict that $[Cu(NH_3)_4]^{2+}$ is square planar, or reproduce tetragonal distortion in Cu(II) complexes. Semi-empirical calculations appear also to be poor at reproducing the more subtle energetic aspects of complex formation such as inductive effects in complexes. Clearly, much work still needs to be done on these types of models before they can be used reliably and realize their full potential in CC. The main cause of the difficulty in developing semi-empirical parameters for metal atoms for modeling coordination compounds appears to be that parameter development has been focused on gas phase formation energies of simple compounds such as fluorides or sulfides, and little attention has been paid to more complex substances, particularly the structural aspects thereof. What is clearly needed is collaboration between theoretical chemists attempting to parameterize semi-empirical models of complexes of metal ions, and inorganic chemists with the background to identify the core aspects of the chemistry that must be reproduced for the semi-empirical model to have any value. *Ab initio* calculations appear to be more successful at modeling coordination compounds, and can yield some truly impressive results. *Ab initio* calculations will

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reproduce the fact that $[Cu(NH_3)_4]^{2+}$ is square planar, or that $[Ag(NH_3)_2]^+$ is linear, and will shed extra added ammonia ligands. *Ab initio* calculations also model inductive effects quite well, which is true even for calculations employing a small basis set, showing that the poor performance of semi-empirical calculations is not due to the fact that they employ a small basis set. However, the computing power needed for anything but relatively simple coordination compounds makes *ab initio* calculations impractical for many more complex systems, so that MM will continue to play an important and growing role in CC. This will be particularly true for biological systems where the metal ions are associated with large biomolecules. The models used in MM and in CC will also continue to improve in the sophistication of their parameterization for modeling steric effects, as well as in addition of electronic aspects such as the ability to predict the extent of tetragonal distortion or the energies of electronic transitions.

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