

Environmental Management Science Program

Project ID Number 55223

De Novo Design of Ligands for Metal Separation

Dr. Garland R. Marshall
Washington University
700 South Euclid Avenue
St. Louis, Missouri 63110
Phone: 314-362-1567
E-mail: garland@ibc.wustl.edu

June 1, 1998

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Research Objective

Develop computer-aided molecular design technology for ligands useful in metal separations. This includes force field parameterization of different metals in various oxidation states and de novo design of ligands optimized for specific metals including constraints to certain chemical classes of ligands.

Research Progress and Implications

This report summarizes year two of a 3-year project and focuses on force field parameterization.

Work continues on the modification of algorithms to construct metal-binding ligands from molecular fragments. The lack of an appropriate theoretically derived functional form for d-orbitals in molecular mechanics has hampered efforts to utilize these programs and our efforts have focused on correcting this deficiency in collaboration with Prof. Anders Carlsson of the Department of Physics as follows:

Our approach for parametrization of transition metal atoms is to fit an empirical potential for molecular mechanics to the potential energy surface calculated by ab initio methods. Conventional ab initio methods¹ using Hartree-Fock theory are known to give good results for most organic molecules. Coordination compounds require the use of high-level basis functions such as triple zeta valence (TZV) to get accurate results which are highly time consuming thus restricting the ligand sizes. In order to overcome these difficulties, the density functional model²⁻⁴, which is known to give results in parallel to the popular MP2 model was used.

The d-electron energy function plays an important role in transition metal complexes. Recently, an energy function for d-electrons has been derived at Washington University based on quantum mechanical analysis.⁵ The d-shell energetics is described via the 'ligand field stabilization energy', which is given by

$$E_{LFSE} = - \sum_{ij} e(r_i) e(r_j) U(q_{ij}) \quad (1)$$

$e(r_i)$, $e(r_j)$ are the coupling strengths of the individual ligands and the q_{ij} is the ligand-metal-ligand angle. $U(q_{ij})$ is an angular function defined as,

$$U(q_{ij}) = [P (\cos q_{ij})^2 - (1/5)],$$

$$\text{where } P = (3 \cos^2 q - 1) / 2.$$

The functional forms of the coupling strengths can be derived from the half-width, W , of the d-complex. The term W is related to the energies of the occupied and the empty d-orbitals by the following term;

$$\bar{5}W^2 = \hat{A} (\bar{E}_n - \bar{E})^2$$

\bar{E}_n is the energy of the occupied d orbitals and \bar{E} is the average energy of the occupied and unoccupied d orbitals.

In order to derive the functional form of W and coupling strengths, ab initio and density functional calculations were performed on various metal complexes. We have initially studied square planar and tetrahedral metal ammonia ($Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}$) and copper-imidazole complexes.

Geometry optimizations were performed at UHF for open shell systems and RHF for closed shell systems, using triple zeta valence (TZV) basis set in ab initio and BP/DN* in density functional model. Optimized geometries for the Cu⁺²-imidazole complex shows good agreement with known crystal structures.

The variation of half width with respect to metal ligand distance was then computed by varying the metal-ligand distances. Detailed studies have been carried out for Cu-ammonia and Cu-imidazole complexes. The exponential functional form of the coupling strength was then derived from least squares fit and the value of W(*) was optimized so that the sum of the squares of the error is minimum around the equilibrium distance. The following function is obtained from the least squares fit;

$$W(r) = W(*) + b e^{-a r}$$

W(r) is the half width at a particular metal-ligand distance r.

The best least squares fit gave a value of 0.035 Hartrees for W(*), the coefficient b is 0.19378 Hartrees and the exponent is 1.79108 Å⁻¹ for the Cu-ammonia and Cu-imidazole complexes. Further studies for various other combinations of metals and ligands are underway. Some of our preliminary studies have shown that the parameter W varies not only with the metal-ligand distance, but also with the varying ligands.

The importance of the angular term in the equation (1) can be understood by comparing the energetics of the square planar vs the tetrahedral geometries. The computed energy differences for the square vs tetrahedral complexes show the magnitude of angular term changes and hence the preference for a particular geometry which varies depending on the central metal atom.

Planned Activities

It is our intent to validate the force field parameters for various metals of interest by modeling a variety of known complexes which were not used in parameter development. These parameters will then be included in the TINKER modeling package which is available over the internet. They will also be incorporated into our de novo design software and ligands designed to be selective for various metals of interest. This will be accomplished in the remaining year of the project.

Other Access To Information

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