

Environmental Management Science Program

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Architectural Design Criteria for F-Block Metal Ion Sequestering Agents

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Research Objective

The objective of this project is to provide a means to optimize ligand architecture for f-block metal recognition. Our strategy builds on an innovative and successful molecular modeling approach in developing polyether ligand design criteria for the alkali and alkaline earth cations. The hypothesis underlying this proposal is that differences in metal ion binding with multidentate ligands bearing the same number and type of donor groups are primarily attributable to intramolecular steric factors. We propose quantifying these steric factors through the application of molecular mechanics models.

The research involves close integration of theoretical and experimental chemistry. The experimental work entails synthesizing novel ligands and experimentally determining structures and binding constants for metal ion complexation by series of ligands in which architecture is systematically varied. The theoretical work entails using electronic structure calculations to parameterize a molecular mechanics force field for a range of metal ions and ligand types. The resulting molecular mechanics force field will be used to predict low energy structures for unidentate, bidentate, and multidentate ligands and their metal complexes through conformational searches. Results will be analyzed to assess the relative importance of several steric factors including optimal M-L length, optimal geometry at the metal center, optimal geometry at the donor atoms (complementarity), and conformation prior to binding (preorganization). An accurate set of criteria for the design of ligand architecture will be obtained from these results. These criteria will enable researchers to target ligand structures for synthesis and thereby dramatically reduce the time and cost associated with metal-specific ligand development.

Research Progress and Implications

Substantial progress has occurred in the first eighteen months of this project. Our research to date has focused on the amide functional group. We have synthesized twenty multidentate amide ligands ranging from simple diamides such as tetraalkylmalonamides to more complicated calixarene derivatives. The coordination chemistry of these ligands with actinides and lanthanides is under investigation. Solution phase stoichiometries for metal diamide complexes have been determined by infrared spectrophotometric titrations and by solvent extraction results. In the majority of cases the same stoichiometries were observed in the solid state using thermal gravimetric analysis and single crystal X-ray diffraction. Fourteen novel structures have been obtained. These include the first crystal structures of lanthanide succinamide complexes, revealing a rich and varied coordination chemistry for this diamide.

A variety of methods for the determination of metal amide binding constants have been investigated. Calorimetry has yielded the first binding constants for diamides with any metal ion. Binding constants for 1:1 ligand:metal complexes have been measured for six diamides with trivalent europium, quantifying a significant effect of ligand architecture on complex stability. Similar effects were obtained with a solvent extraction method, confirming the calorimetry results. Solvent extraction studies also

have yielded the first example in which calixarene conformation is observed to effect the extraction of the uranyl ion.

An extended MM3 model has been developed for metal amide complexes. Force field development has required the refinement of existing amide parameters and the generation of new parameters for the metal-amide interactions. This has been accomplished using both electronic structure calculations and experimental data (crystal structures). We have found that each metal requires a different set of parameters. A unique feature of the parameterization is that the metal-dependent parameters are correlated with metal ion properties. Thus, the model can be applied to any metal ion in the Periodic Table. The performance of the model has been validated by comparison of calculated and observed structural features. A total of 56 crystal structures were used in this comparison including amide complexes with alkaline earth, transition metals, lanthanides, and actinides. A marked difference was observed in amide orientation with transition metals when compared to the f-block metals. This observation provides criteria to design amide ligand architecture with optimal complementarity for actinides.

Planned Activities

Our research program will focus on the amide function group for the rest of this year and into FY99. Characterization of actinide diamide complexes is in progress. Additional succinamide derivatives will be prepared to evaluate the effect of the degree of bridge alkylation. The structure-function data sets in diamides will be expanded by the continued application of calorimetry and solvent extraction methods to measure additional binding constants. Additional calixarene amides will be prepared and characterized.

Conformational analyses of malonamide and succinamide derivatives is in progress. All geometries and relative energies obtained with the model will be verified by geometry optimizations and frequency calculations obtained from electronic structure calculations. Ligand strain energies will be evaluated for all the diamides for which binding affinities have been measured. Comparison of binding affinity with ligand strain will indicate to what extent ligand steric demands influence complex stability. The results of this study will be used evaluate the extent of improvement that can be obtained by the structural modification of diamides.

Other Access To Information

Further details on this research are available in progress reports PNNL-11589 and PNNL-11899. Results of this research have been presented in fifteen talks at scientific conferences and are documented in thirteen publications:

- (1) Falana, O.M.; Koch, H.R.; Roundhill, D.M.; Lumetta, G.J.; Hay, B.P. "Synthesis and Extraction Studies of 1,2- and 1,3-Disubstituted Butylcalix[4]Arene Amides with Oxyions: Geometric and Conformational Effects." *J. Chem. Soc. Chem. Commun.* 1998, 503-504.
- (2) Hay, B.P.; Clement, O. "Metal Complexes" in *Encyclopedia of Computational Chemistry*, P. von Rague Schleyer, Editor-in-Chief, John Wiley and Sons, London, in press.
- (3) Clement, O.; Rapko, B.M.; Hay, B.P. "Structural Aspects of Metal-Amide Complexes." *Coord. Chem. Rev.*, in press.
- (4) Rao, L.; Xia, Y.; Rapko, B.M.; Martin, P.F. "Synergistic Extraction of Eu(III) and Am(III) by Thenoyltrifluoroacetone and Neutral Donor Extractants: Octyl(Phenyl)-N,N-Diisobutyl-carbonyl-methylphosphine Oxide and 2,6-Bis(Diphenylphosphino)methyl Pyridine N,P,P Trioxide." *Solv. Extr. Ion. Exch.*, in press.
- (5) Yordanov, A.; Roundhill, D. M. "Solution Extraction of Transition and Post-Heavy and Precious Metals by Chelate and Macrocyclic Ligands." *Coord. Chem. Rev.*, in press.
- (6) Lumetta, G.J.; Rapko, B.M.; McNamara, B.K. "Using Excel" to Analyze Liquid-Liquid Extraction Equilibria." *J. Chem. Ed.*, submitted.
- (7) Wolf, N.J.; Georgiev, E.M.; Yordanov, A.T.; Whittlesey, B.L.; Koch, H.F.; Roundhill, D.M. "Synthesis of Lower Rim Amine and Carbamoyl Substituted Calixarenes as Transfer Agents for Oxyions between an Aqueous and a Chloroform Phase." *Inorg. Chem.*, submitted.
- (8) Yordanov, A.T.; Wolf, N.J.; Georgiev, E.M.; Koch, H.F.; Falana, O.M.; Roundhill, D.M. "Derivatized Calix[4]arenes as Selective Phase Transfer Extractants for Heavy Metal and Oxyion Salts." *Comm. Inorg. Chem.*, submitted.
- (9) McNamara, B.K.; Lumetta, G.J.; Hay, B.P.; Rapko, B.M.; and Rogers, R.D. "Coordination Chemistry of Lanthanide Nitrates with N,N,N,N-Tetramethylsuccinamide." *Inorg. Chem.*, submitted.
- (10) Hay, B.P.; Clement, O.; Sandrone, G.; Dixon, D.A. "A MM3(96) Force Field for Metal-Amide Complexes." *Inorg. Chem.*, submitted.

- (11) Sandrone, G.; Dixon, D.A.; Hay, B.P. "C(sp²)-C(sp³) Rotational Barriers in Simple Amides: H₂N-C(=O)-R, R = Methyl, Ethyl, i-Propyl, t-Butyl." J. Phys. Chem. submitted.
- (12) Rao, L.; Zanonato, P.; Di Bernardo, P. "Studies of Europium(III) Complexation with Tetramethylmalonamide and Tetramethylsuccinamide in Organic Solvents by Calorimetry and Optical Spectroscopy." Inorg. Chim. Acta, manuscript in preparation.
- (13) Dixon, D.A.; Sandrone, G.; Hay, B.P. "Computational Studies of Cation Binding to Amides. I. Proton Binding Affinity." J. Phys. Chem., manuscript in preparation.