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Project Title: **Architectural Design Criteria for F-Block Metal Ion Sequestering Agents**

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Architectural Design Criteria for f-Block Metal Sequestering Agents

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Research Objective

The objective of this project is to provide the 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 proposed 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.

Problem Statement

Critical tasks in the cleanup of U.S. Department of Energy (DOE) sites include processing radioactive wastes for disposal in long-term storage, remediation/restoration of environmental sites resulting from radioactive contamination, and decontamination/decommissioning of nuclear facilities. Because the radioactive components, most of which are metals, are typically present in very low concentrations, it is desirable to remove them from the bulk of the contaminated source (process waste stream, groundwater, soil) and concentrate them to minimize the volume of radioactive material destined for permanent subsurface disposal and thus minimize disposal costs. One group of radionuclides, the actinides, which are pervasive throughout the DOE complex, is of special concern. In particular, thorium, uranium, neptunium, plutonium, americium, and curium with half-lives ranging from 10^2 to 10^6 years can all be found in various DOE wastes, contaminated soils and groundwaters, and contaminated facilities. Lanthanide elements are also of concern because they form an important group of fission products that can persist in radioactive wastes for decades (e.g., ^{152,154,155}Eu).

Organic ligands with a high degree of metal ion specificity are essential components for developing separations processes for metal ions. Over the past 50 years, much research has focused on the discovery of selective ligands for f-block metal separations; both neutral and ionic ligands have been examined. Despite past success in the discovery of ligands that exhibit some degree of specificity for the f-block metal ions, the ability to further control binding affinity and selectivity remains a significant challenge to the synthetic chemist. The approach for developing these ligands has involved lengthy and costly experimental programs of organic synthesis and testing, which, in the absence of reliable methods for screening

compounds before synthesis, requires an extensive research effort. Criteria for accurately selecting target ligands would result in much more effective use of resources.

Research Progress

This project combines a theoretical and experimental approach to developing ligand design criteria for selective complexation of f-block metal ions. These criteria will address how to best connect donor functionality to achieve metal ion recognition in multidentate ligands. For the f-block metal ions, donor groups of interest include amides, phosphine oxides, pyridine N-oxides, and catechols. Scoping studies were performed on these ligands during the first year of the project, FY 1997. A decision was made to focus solely on amides. Ligands containing the amide functional group are currently used in DIAMEX (an actinide separation process used for treatment of commercial reprocessing wastes) and TRUEX (actinide separation process under testing for use in tank waste cleanup at Idaho National Engineering and Environmental Laboratory).

The DIAMEX process uses a diamide ligand as the actinide extractant. Diamides such as malonamide and succinamide contain two oxygen donor groups and can form bidentate complexes. A bidentate ligand is the simplest case in which the issue of binding site organization arises. There are three structural variables that can affect binding site organization in a diamide: the length of the bridge between the two amides, the degree of bridge alkylation, and the steric bulk of the alkyl groups attached to the nitrogen. Understanding the effect of these structural variables on metal ion complexation provides criteria for optimizing the performance of multidentate amide ligands. In FY 1999 our research continues to focus on the synthesis and characterization of diamides and their complexes, the development and application of methods to measure ligand binding affinities for f-block metals, and the application of molecular models to these ligands and their metal complexes. The goal is to generate structure-function data and to correlate these data using molecular models. In a parallel effort, Professor D. Max Roundhill is preparing a series of calixarene amides and studying their behavior as metal ion extractants. We plan to use a molecular mechanics model to examine the metal binding site organization in these complex polyamides.

Synthesis and Characterization

We have prepared the diamides **1**–**14** in multigram quantities (see Figure 1). Compounds **5**, **7**, **8**, **12**, **13**, and **14** are previously unreported. All have been characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and GC-MS. These diamides represent the three types of structural variation. The bridge length is varied in **1** and **2**, and in **3** and **4**. The degree of bridge alkylation is varied in **1**, **5**, and **6**, in **3**, **7** and **8**, in **9** and **10**, in **11** and **12**, and in **4** and **13**. The steric bulk of the alkyl groups attached to the nitrogen is varied in **1**, **3**, **9**, **11**, and **14**, in **5**, **7**, and **12**, and in **6** and **8**.

The coordination chemistry of diamides with lanthanides has been explored with emphasis on the parent compounds **1** and **2** (presentation 7, 12, 20, and 23; publication 16, 25, 26, and 27). Solid state structural information was obtained by single-crystal x-ray diffraction at the University of Alabama in the laboratory of Professor R.D. Rogers and thermogravimetric analysis (TGA). The question of whether or not the solid state structures are maintained in solution was addressed through the use of infrared (IR) spectroscopy. The crystal structures determined in this work are shown in Figure 2. We have determined the first crystal structures for **1** with lanthanide nitrates. The La and Nd complexes are isostructural and have the same butterfly arrangement of the two malonamide chelates that has been observed with other malonamide derivatives. However, the Gd complex exhibits a different and previously unreported structural isomer.

TGA analysis reveals that the reaction of lanthanide nitrates with **1** yields 2:1 ligand:metal species for all the lanthanides examined (La, Nd, Gd, and Yb). The structures for La, Nd, and Gd have been determined by single crystal x-ray diffraction and were found to be monomeric with two bidentate chelating diamides, consistent with previous literature reports. Titrations of lanthanide
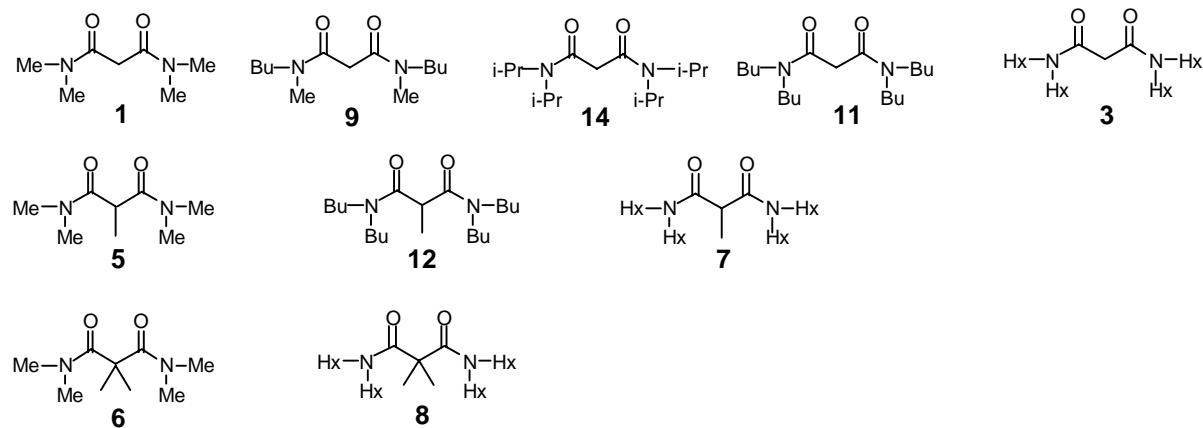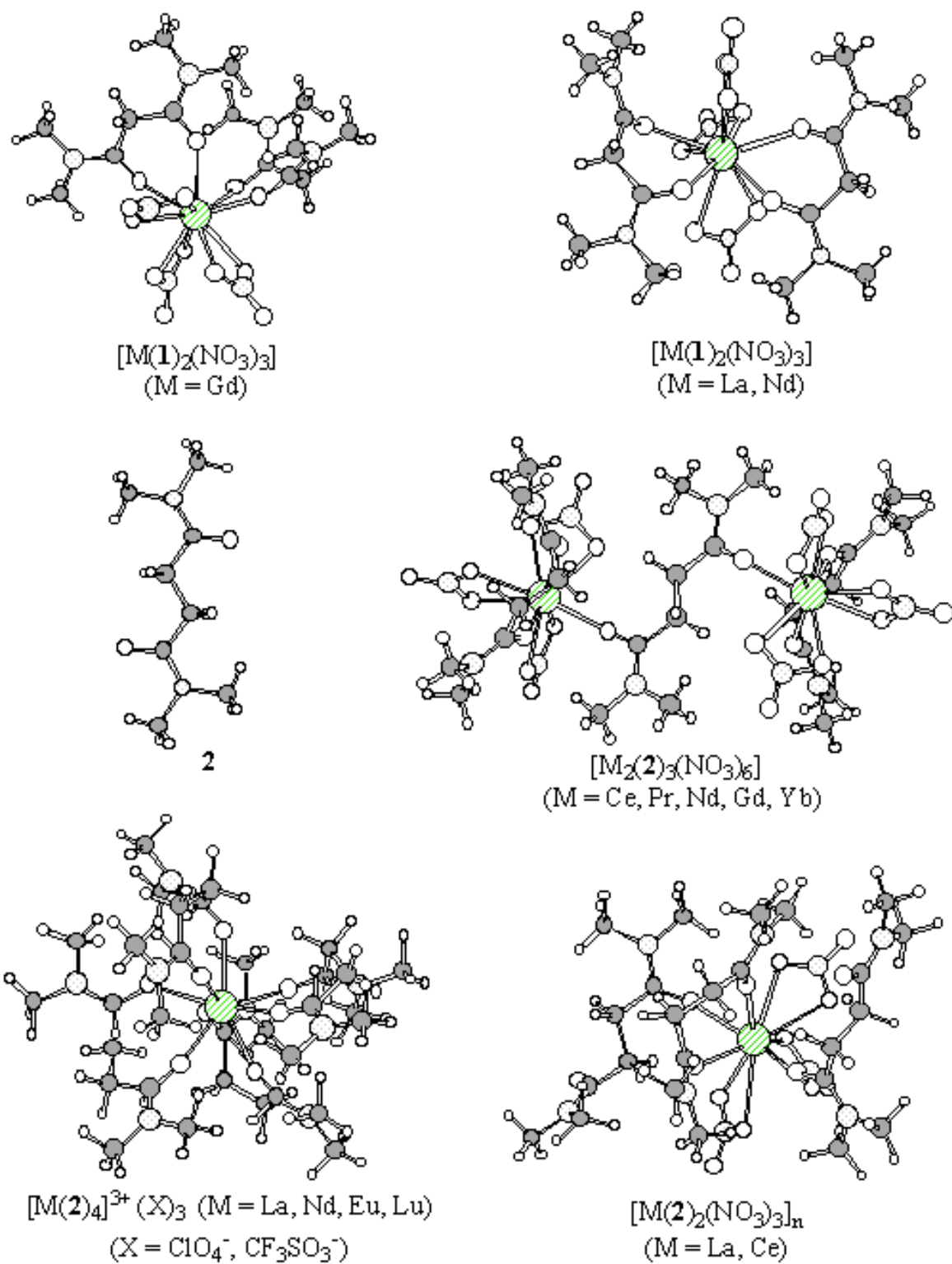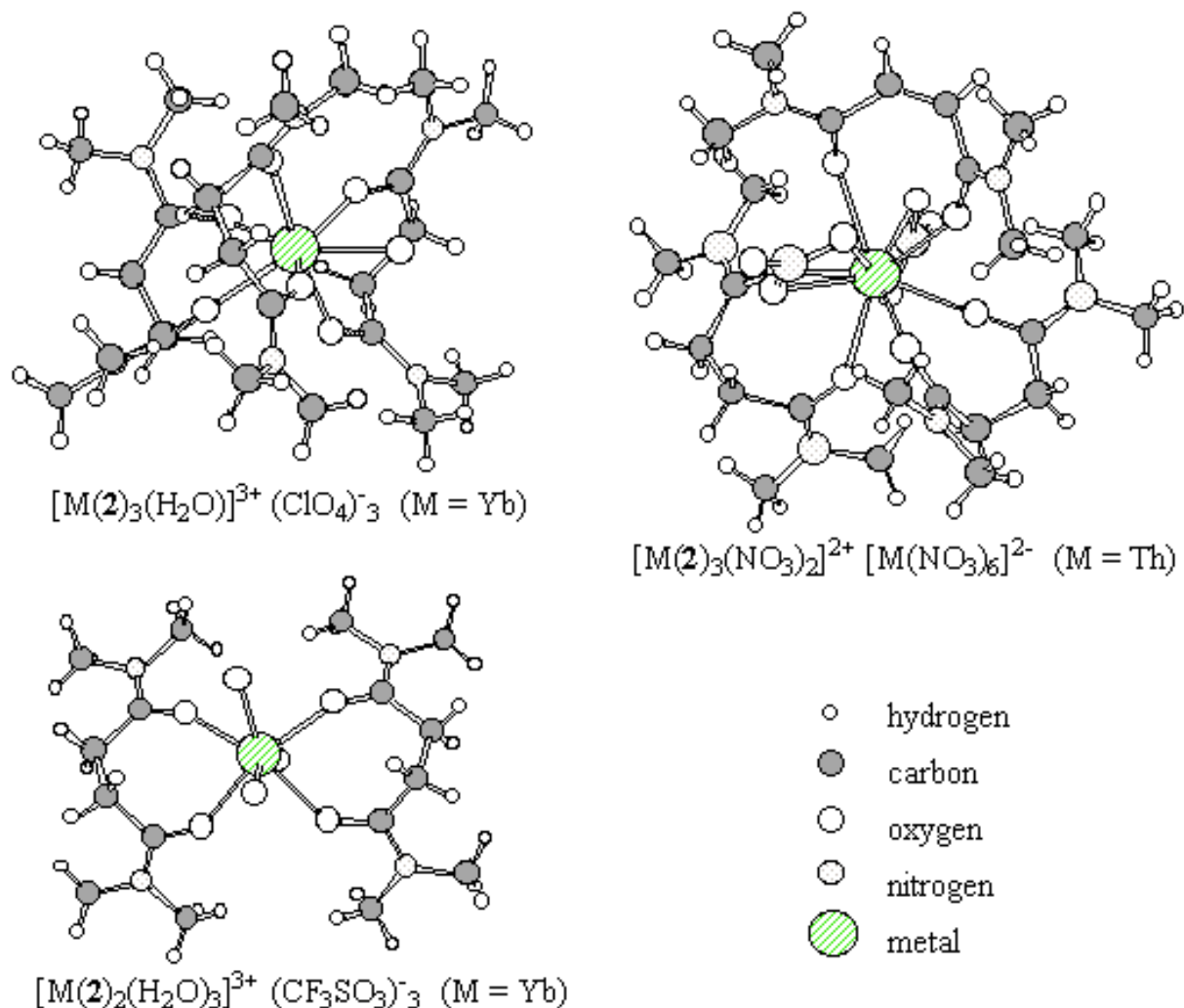
Varied Bridge Length

Varied Bridge Alkylation
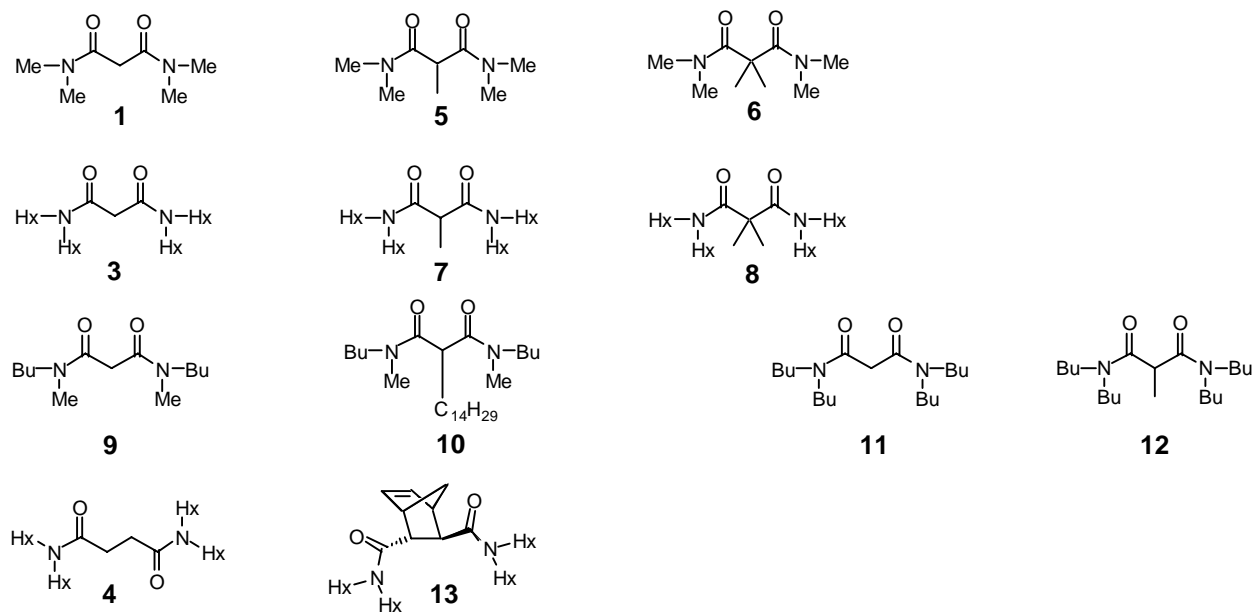
Varied N-Alkylation

Figure 1. Diamide Derivatives Prepared for this Study

$[M(\mathbf{1})_2(NO_3)_3]$
(M = Gd)

$[M(\mathbf{1})_2(NO_3)_3]$
(M = La, Nd)

2

$[M_2(\mathbf{2})_3(NO_3)_6]$
(M = Ce, Pr, Nd, Gd, Yb)

$[M(\mathbf{2})_4]^{3+} (X)_3$ (M = La, Nd, Eu, Lu)
(X = ClO$_4^-$, CF$_3$SO$_3^-$)

$[M(\mathbf{2})_2(NO_3)_3]_n$
(M = La, Ce)

Figure 2. X-Ray Crystal Structures for **2** and Metal Complexes of **1** and **2**

1.106

$[M(\mathbf{2})_3(H_2O)]^{3+}$ $(ClO_4)^-_3$ (M = Yb)

$[M(\mathbf{2})_3(NO_3)_2]^{2+}$ $[M(NO_3)_6]^{2-}$ (M = Th)

○	hydrogen
●	carbon
○	oxygen
○	nitrogen
◉	metal

$[M(\mathbf{2})_2(H_2O)_3]^{3+}$ $(CF_3SO_3)^-_3$ (M = Yb)

Figure 2. (contd)

nitrates with **1** or **3** are consistent with the formation of a 2:1 species in solution as evidenced by the FTIR spectra. No evidence for any higher L:M species is observed.

We have obtained a series of crystal structures for complexes of lanthanides with **2** (see Figure 2). These are the first crystal structures for any lanthanide succinamide complex and reveal that lengthening the bridge leads to a rich and varied coordination chemistry. TGA analyses revealed that a 2:1 ligand:metal species occurs only with the early lanthanides (La and Ce). Single crystal x-ray diffraction revealed a *polymeric* material with one chelating bidentate diamide bound solely to one metal and the second bridging between two metals. IR spectroscopic titration of lanthanide nitrates with **2** is consistent with the formation of a 2:1 species in solution with no evidence for any higher L:M species.

TGA analysis reveals a different stoichiometry, a 3:2 ligand to metal ratio, for complexes of **2** with the lanthanides Pr, Nd, Gd, Yb, and Lu. The structures of the Pr, Nd, Gd, and Yb compounds have been determined by single crystal x-ray diffraction and were found to be *dimeric*, with one bidentate diamide

bound to a single metal and a bidentate diamide bridging two metals. Curiously, a crystal containing this stoichiometry was also isolated for Ce. With the exception of La and Ce, IR spectroscopic titration of lanthanide nitrates with **2** or **4** is consistent with the formation of the 3:2 species in solution with no evidence for any higher L:M species.

Ce appears to be a special (and transitional) lanthanide in its reaction with **2**. Although IR and TGA analysis indicate it is predominantly the 2:1 ligand-to-metal product, crystals for both the 2:1 and 3:2 compound were isolated. No evidence was found for multiple stoichiometries with any of the other lanthanides.

If non-coordinating counteranions are present, such as triflate or perchlorate, TGA analysis of the products formed in the presence of excess **2** reveals a 4:1 ligand: metal complex with Eu and Nd. Single crystal x-ray diffraction revealed a monomeric species with four bidentate chelating diamides. IR spectroscopic titration of lanthanide perchlorates with **2** is consistent with the formation of a 4:1 species in solution with no evidence for any higher L:M species. However, this stoichiometry is very sensitive to the amount of water present. By controlling the concentration of water, it is possible to isolate mixed aquo/diamide complexes such as those shown in Figure 2.

Binding Affinities

A literature search was performed to locate any information regarding single-phase stability constants for amide complexes of lanthanides or actinides and solution structural information on such complexes. This search revealed that not only are there no existing structure-stability data sets but no stability constant data for f-block metal ions with pure amide ligands. Given that the amide group is neutral over a wide pH range, this situation reflects the general difficulty of determining stability constants for non-ionizable ligands. Generation of structure-function data require that the relative metal binding affinities should be determined under identical experimental conditions of solvent, counter ion, and temperature. A variety of methods for the determination of metal-amide binding constants were investigated in first year of this project. These methods include electronic spectroscopy, IR spectroscopy, use of ion selective electrodes, calorimetry, and solvent extraction. Of these methods, solvent extraction and calorimetry were found to be the most applicable.

Calorimetry has yielded the first measurements of diamide binding constants with any metal ion (presentations 4, 5, 18; publication 30). The formation constants for 1:1 ligand:metal complexes have been determined for $Eu(ClO_4)_3$ with **1**, **2**, **3**, **8**, **9**, and **14** in 10% DMSO/90% acetonitrile solution buffered to ionic strength 0.1 M at 25°C. The results are presented in Table 1. A decrease in the formation constant by a factor of 3.7 occurs on lengthening the bridge by one methylene group, as shown in the comparison of **1** and **2**. Comparing **3** and **8** demonstrates that dialkylation of the methylene bridge causes a drop in the formation constant of at least 2 orders of magnitude. Data for **1**, **3**, **9**, and **14** illustrate that the formation constant steadily decreases as the steric bulk of N-alkyl groups increases.

Table 1. Formation Constants for $Eu(ClO_4)_3$

Ligand	Formation Constant, M^{-1} ($\pm 3\ \sigma$)	
1	21.9	(1.1)
2	5.9	(1.2)
3	3.5	(1.3)

8	<0.1	
9	11.0	(1.2)
14	1.2	(1.2)

Solvent extraction has also yielded structure-function data for diamide complexes with europium and uranyl nitrates. We have developed a new computer program, the SX Solver, to analyze solvent-extraction equilibria (publication 8). The program operates out of Microsoft Excel® and uses the built-in "Solver" function to minimize the sum of the square of the residuals between measured and calculated distribution coefficients. This program has been used to analyze europium and uranyl extraction data, as discussed below.

The extraction of europium(III) nitrate from aqueous acidic nitrate solutions with a series of tetrahexylmalonamides in t-butylbenzene has been investigated (presentation 7, 21; publication 14). The tetrahexylmalonamides considered were **3**, **7**, and **8**. This series of ligands allowed for a systematic determination of the effects of alkyl substitution of the methylene carbon. Equilibrium modeling of the extraction data indicates that there is only one species present in all cases, $Eu(L)_3(NO_3)_3$. The extraction constant decreases by seven-fold in going from **3** to **7**. However, a precipitous drop in the extraction constant occurs on going from **3** to **8**, i.e., with substitution of a second methyl group on the methylene carbon (see Table 2). This drop is consistent with the calorimetry results suggesting that the effect is due to the metal ligand interaction rather than environmental factors such as counteranion, solvent, or concentration.

The extraction of uranyl nitrate aqueous acidic nitrate solutions with **3**, **7**, and **8** in t-butyl-benzene also has been investigated (presentation 21, publication 13). Equilibrium modeling of the extraction data indicates that there are up to three different species present. These are $UO_2(NO_3)_2L$, $UO_2(NO_3)_2L_2$, and $UO_2(NO_3)_2L_3$. The relative population of these species depends on the nitrate concentration and the identity of the ligand. Extraction constants for the $UO_2(NO_3)_2L_2$ species could be determined for all three ligands (see Table 2). The relative binding affinities parallel those observed for europium complexation.

Table 2. Malonamide Extraction Constants (3.0 M NaNO$_3$)

Ligand	K_{ex} (europium)	K_{ex} (uranyl)
3	0.041	50.4
7	0.0057	29.5
8	<0.0002	1.2

The stoichiometries $Eu(L)_3(NO_3)_3$ and $UO_2(NO_3)_2L_2$ are inconsistent with the generally accepted bidentate coordination of the diamides and nitrate counteranions. However, these stoichiometries are consistent with the formation of complexes with monodentate-bound diamides. Several lines of evidence support this supposition. First, we have found that the same extraction stoichiometries found with the malonamides also are observed with the monoamide N,N- dihexylbutamide. Second, in accord with the well-known chelate effect, a bidentate ligand should exhibit binding constants several orders of magnitude greater than a unidentate ligand. However, under identical experimental conditions the extraction constant for the diamides is only a factor of two greater than the monoamide for both uranyl and europium. Third, although there are no structurally characterized examples of diamide complexes with the observed

extraction stoichiometries, there is ample precedent for these stoichiometries with monoamides. Finally, molecular modeling studies reveal that the trends observed following alkylation of the central methylene are inconsistent with bidentate coordination but are consistent with monodentate coordination by the diamide (*vide infra*).

Calix[4]arene Amides

A series of eight calixarene amide derivatives have been prepared and characterized in the laboratory of Professor D.M. Roundhill at Texas Tech (publications 2, 6). Solid-phase structures for two of these compounds have been determined by single crystal x-ray diffraction (publication 6). The use of these ligands as metal ion extractants is under investigation (presentations 8, 9, 22; publications 2, 6, 9, 19 - 21). For example, geometrically isomeric 1,2- and 1,3-tert-butylcalix[4] arene amides disubstituted with (dibutylcarbamoyl)methoxy groups have been structurally characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Two non-interconverting conformers of the 1,2-isomer have been isolated. The 1,3-isomer and the two 1,2-isomers have been used to extract the uranyl ion into toluene and isooctane. The degree of the extraction depended on the particular conformer of the calixarene. As highlighted in a science/ technology concentrate in C&E News, March 2, 1998, this is the first example in which such conformer effects on the extraction of the uranyl ion have been observed.

Modeling

Our approach uses a molecular mechanics model to relate ligand structure to metal ion binding affinity. Precedence for this approach is documented in an exhaustive review of applying molecular mechanics to obtain structure-function relationships in coordination chemistry (presentation 17, 18; publication 3, 18). Using a molecular mechanics model requires the development of an extended force-field to handle the specific system under study. In this case, 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 with the MM3 force field using both electronic structure calculations and experimental data (crystal structures).

To understand how ligand architecture affects metal ion complexation, it is imperative to first understand the structural features of the free ligand. Given the importance of the amide functional group in organic chemistry and biochemistry, we were surprised to discover how little was known about the shape of simple amides and diamides. We found that the widely used and extensively validated MM3 model failed to produce observed ligand conformations. To address this problem, we first performed ab initio density functional theory (DFT) and molecular orbital theory calculations to obtain the rotational potential surfaces for C_a-C bond rotation in acetamide, propanamide, 2-methylpropanamide, and 2,2-dimethylpropanamide (see Figure 3). These data were used to correct the MM3 model. The refined model now predicts the correct shapes for amides (presentation 10, publication 12).



acetamide   propanamide   2-methylpropanamide   2,2-dimethylpropanamide
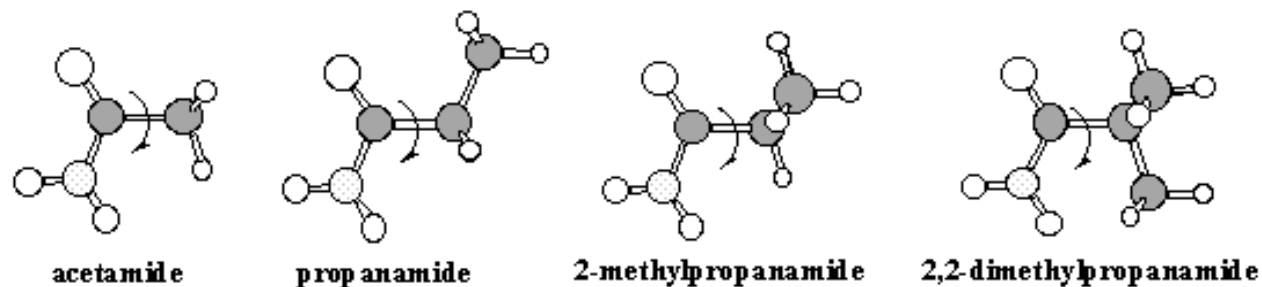
Figure 3. Illustration of the C_a-C Bond Rotations Investigated in Simple Amides

The MM3 force field did not contain torsional parameters needed to describe bond rotations present in malonamides. Therefore, we generated data needed to develop these parameters. This involved ab initio DFT and molecular orbital theory calculations to identify all stable conformations of malonamide, the three geometric isomers of N,N-dimethylmalonamide, and N,N,N',N'-tetramethylmalonamide, **1** (publication 17). Two stable conformations were identified for each malonamide derivative (see Figure 4). Only one of these ten structures had previously been reported. We then adjusted the MM3 model parameters to reproduce the structures and relative energies from the electronic structure calculations.
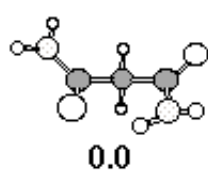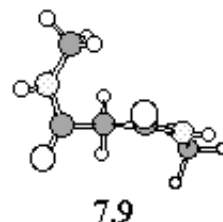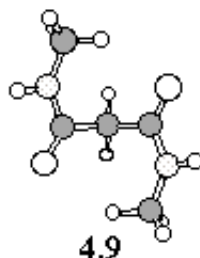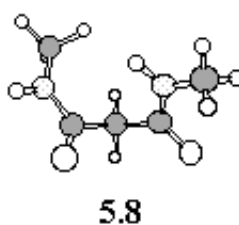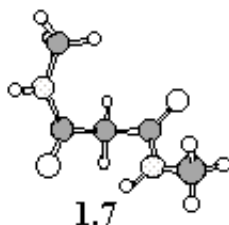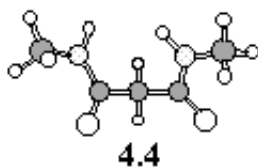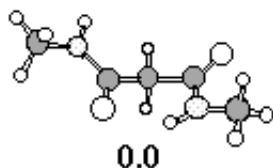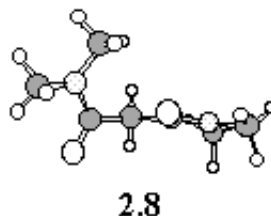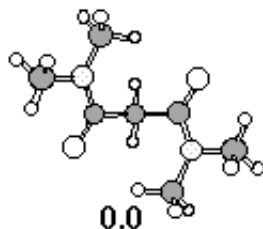

Figure 4. Malonamide Structures and Relative Energies (kcal/mol) from MP2/pTVZ Calculations

We also examined the conformations of N,N,N'N'-tetramethylsuccinamide, **2**, to identify the low energy shapes of this ligand and to provide a benchmark for the MM3 model performance (publication 23). Unlike the malonamide, **1**, which exhibits only two stable conformations, MM3 calculations revealed that **2** has at least 18 minima (see Figure 5). Electronic structure calculations were performed on these 18 minima. MM3 and DFT/DZVP structures and energies were in general agreement. However, the energies of several MM3 conformations were significantly different than those obtained by the electronic structure calculations. Examination of these cases led to the discovery of a previously unrecognized intraamide interaction.
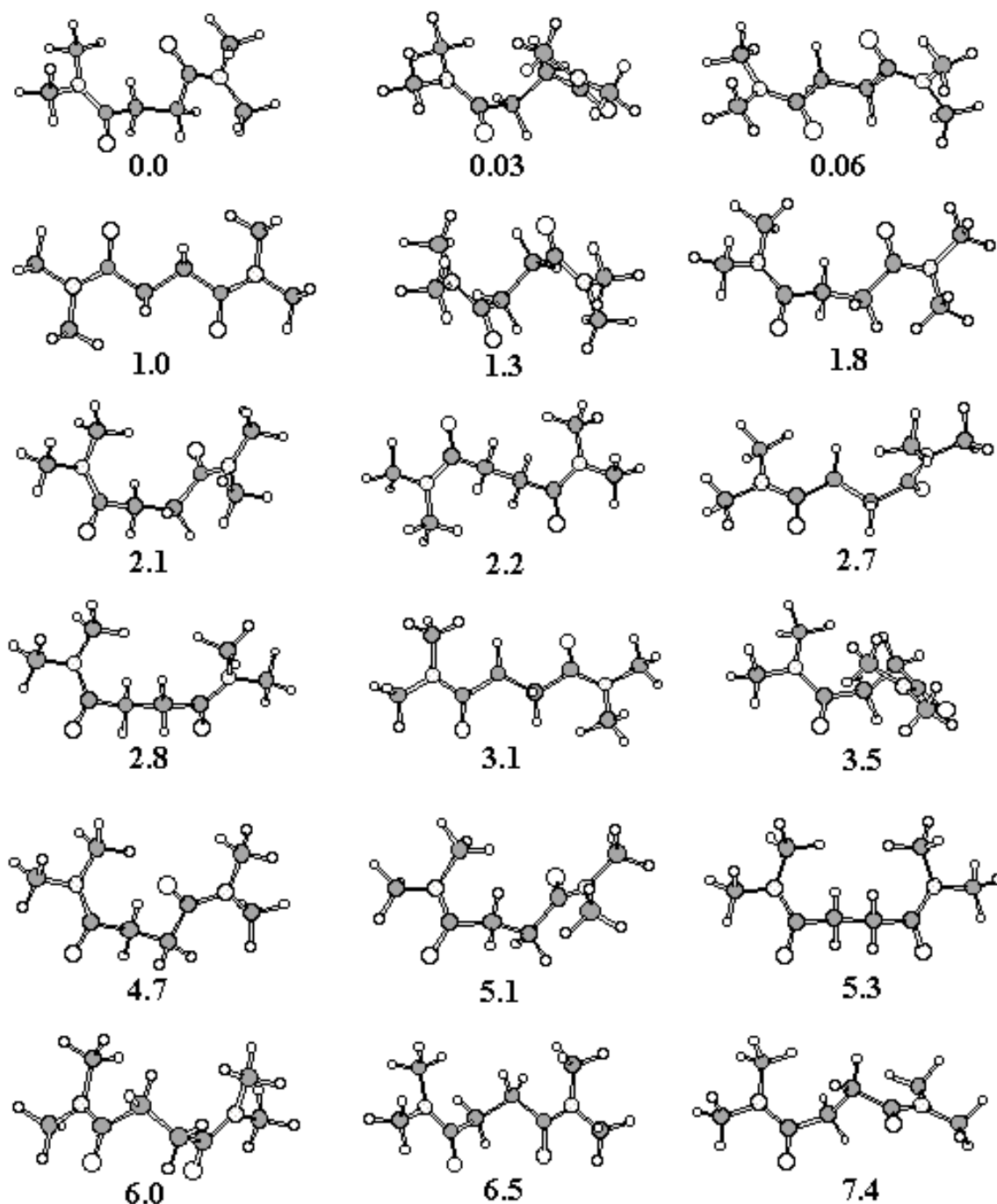
Figure 5. Succinamide Structures and Energies (kcal/mol) from BLYP/DZVP Calculations

We observed that the discrepancies between MM3 and DFT/DZVP energies in the succinamide structures occurred when there were close contacts (• 2.3 Å) between the methyl hydrogens and the oxygen atoms. This suggested the possibility of intramolecular hydrogen bonding between these groups. To test this hypothesis, calculations were performed on dimers of the dimethylformamide (see Figure 6). The results confirm the presence of C-H--O interactions. The energy per hydrogen bond, 1.6 kcal/mol, was unexpectedly strong. This previously unrecognized interaction may play an important role in controlling the shape of other polyamides, e.g., proteins (publication 22).
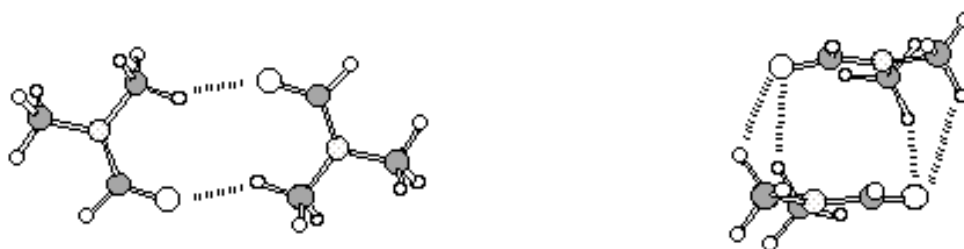
Figure 6. The C-H--O Interactions in Dimethylformamide Dimers

In addition to parameterization for free amides and diamides, we also have developed MM3 parameters for metal-amide interactions. Because the design of selectivity involves both an affinity for the target metal and a rejection of competing metal ions, the MM3 model needed to be applicable not only to f-block metals but also to other metals. For this reason, our model has been designed to evaluate amide complexes with metal ions throughout the periodic table. Ab initio DFT and molecular orbital theory calculations have been used to examine the structure, vibrational modes, and bonding of the various cations to simple unidentate and bidentate amides (publication 28 and 29). These calculations yielded ground state geometries and potential energy surfaces that provided a starting point for the refinement of the MM3 parameters through empirical fitting to crystal structure data, as described below. Because of their expense, the electronic structure calculations were focused on simple complexes of representative metal ions selected to cover a range of charge, size, and metal electronic configuration. Density functional theory has been used to calculate the structures of a variety of amides and metal ion complexes at local and nonlocal levels with at least polarized valence double zeta basis sets. Frequencies have been calculated for all species to determine if they are minima and as an aid in calibrating force field development. These calculations have been done with the computer codes NWChem and DGauss. This work has provided extensive testing of the new code NWChem developed at the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at PNNL.

Initial parameters obtained through electronic structure calculations have been refined to give the best fit to crystal structures. An exhaustive survey of the Cambridge Structural Database identified suitable metal-amide structures for MM3 parameter refinement and validation. In addition, a statistical analysis of bond lengths, bond angles, and torsion angles was performed as a function of the degree of alkylation of the amide functional group and the type of metal ion in the amide complex. Geometric preferences of the coordinated amide ligand were evaluated in terms of M-O-C bond angles and M-O-C-N torsion angles. This evaluation led to the first recognition of the geometric requirements for amide binding (publication 4). A marked difference was observed in the structural features of covalent metals versus ionic metals (see Figure 7). In the covalent metals, the M-O-C angle is close to 120° as would be expected for optimal interaction with the oxygen sp2 orbital. In ionic metals, the M-O-C angle approaches 155°, consistent with

an optimal orientation with the amide dipole. This structural difference suggests that ligand architecture can be manipulated to optimize selectivity for the actinides over the transition metals.

covalent metal   ionic metal

Figure 7. Illustration of Preferred Metal Ion Orientations with Respect to the Amide Donor

The performance of the extended MM3 model for metal-amide complexes has been validated by comparison of calculated and observed structural features. Fifty-six crystal structures, including those shown in Figure 2, were used in this comparison. In addition to f-block metal ions (lanthanides, Th(IV), U(IV), U(VI)), this set of structures included complexes with alkali, alkaline earth, and transition metals. We found that each metal ion requires a different set of parameters. A unique feature of this parameterization is that the metal-dependent parameters are correlated with the ionic radius, charge, and electronegativity of the metal ion. Therefore, the resulting MM3 model can be applied to any metal ion for which these properties are known. For the 56 crystal structures examined to date, the model computes a mean average deviation of $\pm$ 0.035 Å for M-O bond lengths, $\pm$ 5° for M-O-C angles, and $\pm$ 15° for M-O-C-X torsion angles (X = H, C, or N) (presentations 6, 11, 24; publication 11).

The MM3 model has been used to examine isolated malonamide metal ion chelates. Conformational analyses of complexes of **1** with a variety of metal ions reveal that this ligand forms three stable chelating conformers (see Figure 8). This result is consistent with x-ray crystal structure data that provide examples of all three of these forms. Ligand strain analyses have been performed for isolated chelate rings of **1**, **5**, and **6** with europium and uranyl cations. The results predict that the steric effects associated with methylation of the methylene bridge would give a binding affinity order of **5 > 1 > 6**. This order disagrees with the experimental results (**1 > 5 > 6**) suggesting that bidentate coordination is not occurring under the solvent extraction conditions (*vide supra*). On the other hand, MM3 calculations on complexes in which **1**, **5**, and **6** are monodentate-bound yield results that are consistent with the experimental ordering.

0.0   1.4   2.3
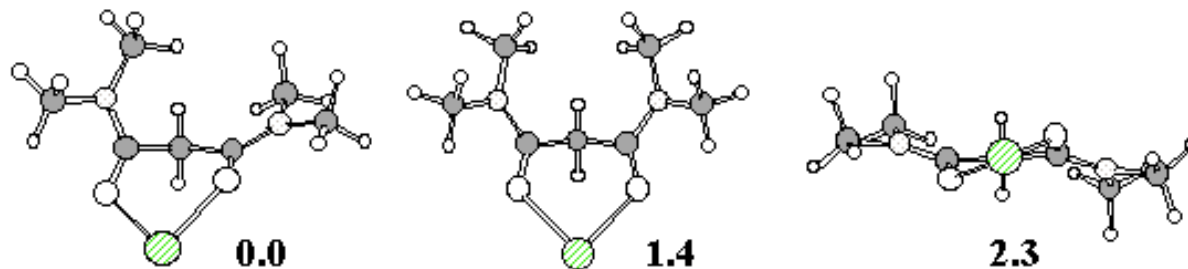
Figure 8. Structures and Energies (kcal/mol) for the Three Conformations of **1** with Am(III)

Examination of the chelate rings formed by **1**, **5**, and **6** in complexes with the f-block metal ions reveals that the oxygen donor atoms in the malonamide architecture are poorly organized for complexation. Significant structural reorganization is required to achieve a binding conformation and the binding conformation does not provide the optimal orientation of either amide with respect to the metal ion. This lack of preorganization and poor complementarity provides an explanation for why these diamides would not form chelates under extraction conditions. Furthermore, these results suggest that alternative ligand architectures, in which the diamide was organized for chelation, could yield significant increases in metal ion binding affinity. Using ligand design criteria developed in this study, we have identified the diamide architecture **15** (Figure 9) that is preorganized for complexation and offers binding sites that are complementary for the trivalent actinides and lanthanides. Synthesis of **15** is in progress at the University of Oregon in the laboratory of Professor Hutchison.

Figure 9. Illustration of **1** and **15** Showing the Optimal Approach Vectors
for Metal Complexation with the Amide Oxygens

Technology Transfer

Publications and presentations of our results have received international attention by scientists interested in f-element separations for nuclear fuel reprocessing. We have received two unsolicited invitations to collaborate. In November 1998, we were visited by Drs. J.-P. Dognon and M.-C. Charbonnel from the Macoule Facility of the Commissariat a L'Energie Atomique (CEA) in France. Dr. Dognon is the manager of the Theoretical and Structural Chemistry Laboratory responsible for the design and development of new extractants for radiochemical separation. This interaction led to the submission of a proposal to the DOE Nuclear Energy Research Initiative in which we would collaborate with the French researchers to develop improved sequestering agents for f-elements. In February 1999, we were visited by Dr. Shoichi Tachimori from the Tokai Research Establishment of the Japan Atomic Energy Research Institute (JAERI). Dr. Tachimori is the director of the Separations Chemistry Laboratory and supervises research on actinide separations. As a result of this visit, negotiations are underway to establish a collaboration interaction between JAERI and the EMSL.

Planned Activities

Our major focus for the remainder of this project is to complete the publication of our results (publications 22–30). In addition, we will attempt to synthesize (in progress at the University of Oregon) and test the preorganized diamide **15**. We also will collect and analyze data on several actinide diamide crystals (in progress at the University of Alabama).

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20. Rapko BM, BK McNamara, RD Rogers, GJ Lumetta, G Broker, and BP Hay. March 1999. "Coordination chemistry of tetraalkyldiamides with f-block metal salts." 217th American Chemical Society National Meeting, Anaheim, California.

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