DALTON
PERSPECTIVE

Molecular modeling of d- and f-block metal complexes

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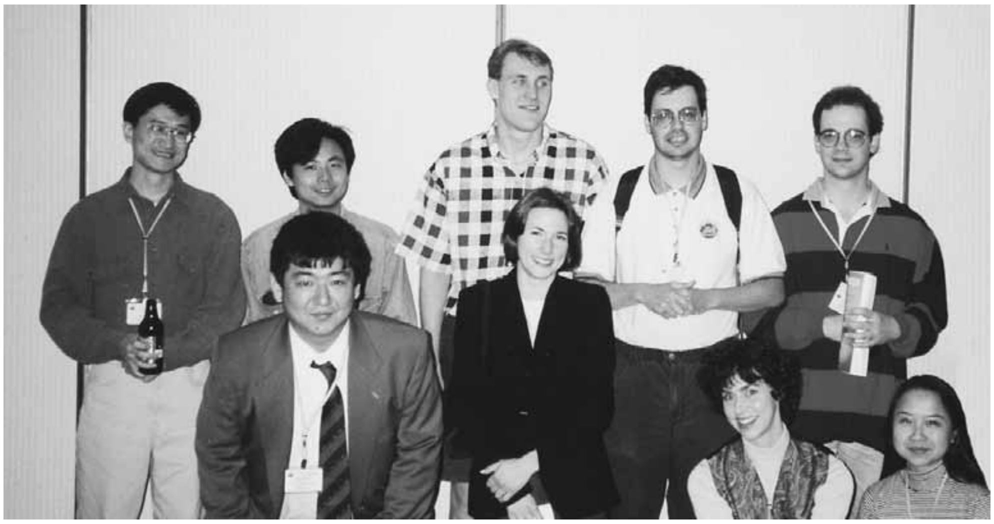
This Perspective gives an overview of challenges in the application of molecular mechanics to d- and f-block complexes. Molecular mechanics (MM) entails a classical mechanics description of chemical systems. Thus, computational challenges faced by the modeler are often different from those encountered for quantum methods. However, as with main group compounds, there are considerable motivations to develop MM force fields for d- and f-block metals. Foremost among these is that MM calculations are very computationally inexpensive. This permits one to (a) study very large (hence generally more experimentally relevant) models, (b) utilize readily available hardware, and (c) carry out more complete conformational analyses. Challenges in the development of MM force fields for d- and f-block metals include (a) the scarcity of metric and vibrational data for parameterization, (b) extending 'organic' force fields to inorganic species, and (c) parameterizing force fields with static structures. However, these problems pale in comparison to the major roadblocks to metal force field development: treating angular distortions about metal atoms (which are more variable than typically seen in lighter main group elements) and transferability (which arises from the tremendous chemical diversity of these metals).

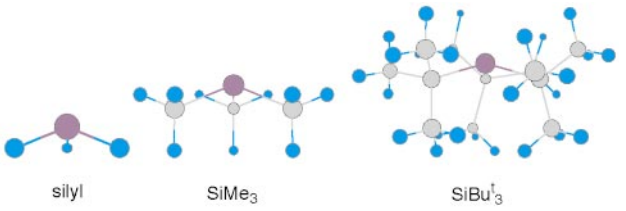
1 Introduction

Perhaps no technological development has made a more significant impact on chemistry in the past two decades than the advent of affordable, reliable, and powerful computers. With these advances, and the development of easy-to-use software, computational chemistry has become a valuable tool in the chemist's arsenal for design and analysis of materials and processes. Although one always runs into the danger of overgeneralizing in a diverse field, one can loosely divide computational chemistry research themes into two general groups: development of new techniques, and extension of existing techniques to new chemical families. This Perspective will focus on the latter, because it is often the case in modeling inorganic chemistry that a good deal of time is spent extending techniques originally developed for organic chemistry.

Computational techniques for modeling inorganic compounds run the gamut of sophistication. In general, the more comprehensive a model (classical or quantal), the greater are the computational resources required. Hence, there is great interest in developing less expensive, although reliable, methods.[1] One approach is the use of semiempirical approximations for a full quantum description of chemical systems. Semiempirical quantum mechanical (SEQM) techniques often involve the approximation or neglect of computationally expensive integrals that describe the interactions among nuclei and electrons.[2] Alternatively these integrals can be viewed as adjustable parameters whose selection is based on the ability to reproduce and ideally predict experimental observables. SEQM methods include the well known extended Hückel method,[3] as well as the techniques included in programs such as MOPAC and recently extended to d-block metals.[2] An alternative approach, the subject of this Perspective, entails a classical mechanics picture of metal complexes.



Tom Cundari obtained his B.S. at Pace University in 1986, and a Ph.D. in 1990 at the University of Florida (Russ Drago, Advisor). After a year of postdoctoral study at North Dakota State University with Mark Gordon, he started as Assistant Professor at The University of Memphis. He was promoted to Associate Professor in 1994. His research interests include modeling of lanthanide and transition metal chemistry, artificial intelligence in inorganic chemistry, and cricket. Pictured in the recent group photo: (back row, left to right) Tie Zhou, Wentao Fu, Tom Klinckman, Tom Cundari and Mike Benson; (front row, left to right) Akihiko Yoshikawa, Leah Saunders, Mary Cocke and Jun Deng.



Scheme 1

2 Goals and Themes

This Perspective will focus on molecular mechanics (MM) techniques for d- and f-block complexes, which signifies a classical ('ball-and-spring') description of chemical bonding. Recent reviews are available describing the development and application of quantum methods for metal chemistry.[4] Excellent overviews of the theory behind MM can be found in reviews by Hay[5] and Landis *et al.*[6] and the monographs by Comba and Hambley[7] and Allinger.[8] The latter deals with organic chemistry but it is requisite reading for anyone wishing to learn MM. Another work that is unfortunately often overlooked is the seminal work by Kepert[9] on metal stereochemistry utilizing a points-on-a-sphere method. It is hoped that this Perspective will serve as an introduction to the challenges and opportunities in MM modeling for inorganic chemists (experimental or computational) who may be more familiar with quantum mechanical techniques.

3 Bigger is Better

Computational chemists have one property in common with gases, they can expand to fill any volume. Hence, a good deal of research involves development of new methods to make feasible the study of larger systems, either with more efficient techniques or the marriage of existing techniques (*e.g.* density functional theory[10]) with more powerful architectures (*e.g.* parallel computing[11]). It seems as if once it becomes feasible to model silyl (SiH_3) substituents, one's experimental colleagues want to model $SiMe_3$ or $SiBu^t_3$, Scheme 1. Larger substituents clearly engender a bigger computational problem, but they are also more experimentally relevant as indicated by a cursory glance at a crystallographic database.[12] There are 3 and 1781 d-block complexes with silyl and $SiMe_3$ substituents, respectively; even the very bulky $SiBu^t_3$ group, developed by Wolczanski group, is found in 17 d-block complexes.[13]

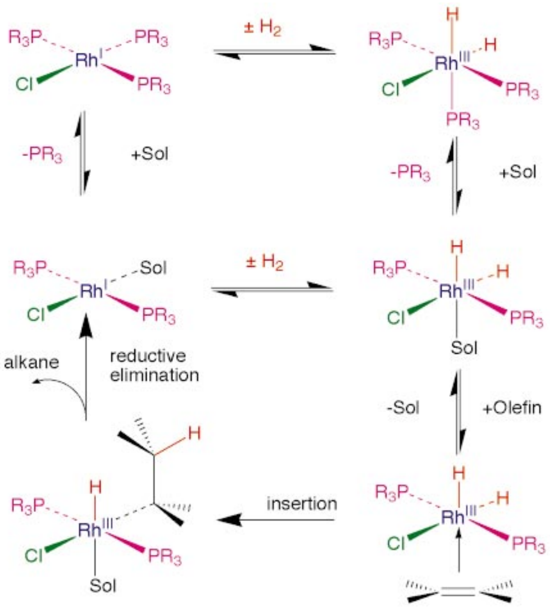
A fruitful approach to efficiently modeling larger systems is molecular mechanics,[5–8] which entails a classical description of a chemical system. In its simplest implementation a complex is viewed as an assemblage of balls and springs, with the former modeling atoms and the latter the chemical bonds that join them. In molecular mechanics the total energy is the sum of individual contributions calculated by means of relatively simple algebraic equations. This is in contrast to the integro-differential equations whose solution in the Schrödinger equation makes quantum mechanical (QM) calculations computationally expensive. This difference immediately suggests that for similarly sized systems MM will be faster by order of magnitudes, which has several important implications.

(1) Molecular mechanics can usually be readily applied to very large systems more efficiently than QM methods. This assertion is supported by the great body of work on the application of MM to large biomolecules.

(2) The reduced computational demands of MM permit the use of less sophisticated (hence less expensive and more readily available) computers to attack chemical problems. This brings with it the potential for nearly all inorganic chemists to employ MM modeling in design and analysis.

(3) Another exciting by-product of studying large systems is that it allows for greater correspondence between experimental systems and computational models. Apart from the obvious fact that more realistic models are preferable, it is useful from a computational point of view. As the model closely approaches experiment, one may assume that substantial deviations (assuming the experimental results are correct!) are due to a deficit in the theoretical model. Although this is unwelcome news for the computational chemist, it is as important to identify systems that are not amenable to description by a model as it is to know those which are.

(4) A major advantage to the routine and efficient study of larger, more experimentally relevant chemical systems is that it allows the theory–experiment interface to be more dynamic. Clearly, if calculations take longer to do than the experiments, there is little advantage to utilizing theory to aid in the design of a new chemical. However, if the modeler can quickly obtain results that yield new insight and provide useful suggestions for further experiments then the synergism between theory and experiment is more fully realized.



Scheme 2 Catalytic olefin hydrogenation mechanics; sol = solvent. Adapted from ref. 15

4 Why Bother?

Before embarking on some of the challenges inherent in MM modeling of d- and f-block metal complexes, it is prudent to discuss motivations for this pursuit lest the reader be unnecessarily disheartened.[14] The d-block or transition metals have fascinated inorganic chemists since the time of the great debate between Jørgensen and Werner regarding the structure of co-ordination complexes. Perhaps the next major revolution in transition metal (TM) chemistry came about with the advent of organometallic chemistry as a distinct discipline. This can be traced to the research of Wilkinson and others with metallocenes and the work of Ziegler, Natta and co-workers on catalytic olefin polymerization. Interest in f-block metals has largely resulted from the utility of the actinides in nuclear chemistry. Recently, there has been growing interest in the lanthanides as experimentalists have sought to exploit their unique chemical, magnetic and photophysical properties for a variety of technological applications.

d-Block complexes are typically found with a wide variety of formal oxidation and spin states, co-ordination geometries, bond types (single, double, triple, quadruple, and dative), and ligand types (hard or soft bases). For the academic chemist unraveling the how and why of this diversity is intrinsically interesting, but it also has a practical side. Consider a typical catalytic cycle (*e.g.* hydrogenation by Wilkinson's catalyst,[15] Scheme 2) with its changing ligand types, co-ordination geometries and oxidation states. The ability of transition metals to stabilize different chemical environments is the reason for their utility in catalysis, advanced materials, biology, and medicine. The diversity provides experimentalists with many options for new materials and processes. However, this chemical diversity can be a thorn in the side of the modeler. To be truly successful a computational model must ideally be able to adequately describe not only a narrow subset of complexes, but rather a wide assortment with comparable accuracy. This challenge brings with it special complications in MM modeling of metal complexes that do not arise in quantum modeling. In the following section I attempt to outline some of these challenges and innovative approaches taken to treat them.

5 The Challenge of Molecular Mechanics for Metal Complexes

The following is a brief overview of molecular mechanics, with emphasis on issues important for metal complexes.[5–7] The interested reader is directed elsewhere for a more in-depth discussion of the theory. A minimal MM force field is given in equation (1).[8] The steric energy (U_{steric}) of a compound is described as the

$$U_{\text{steric}} = \Sigma U_r + \Sigma U_\theta + \Sigma U_\tau + \Sigma U_{\text{vdw}} \quad (1)$$

sum of individual bond-stretching (U_r), angle-bending (U_θ), bond torsion (U_τ), and van der Waals (U_{vdw}) interactions. The optimum geometry is the combination of internal coordinates with the lowest U_{steric}. Additional terms to describe other interactions (*e.g.* hydrogen-bonding or electrostatic interactions) can be added to equation (1) as needed.

A simple MM picture of a molecule as a collection of balls and springs is instructive. A spring is described by Hooke's law, equation (2), which introduces several parameter types. First,

$$U_q = 0.5k(q - q_0)^2 \quad (2)$$

one must know the equilibrium geometry (q_0) of the spring (bond). The second important quantity is the force constant (k) which describes the restoring force needed to bring the spring back to equilibrium. I refer to the former as *metric parameters* and the latter as *vibrational parameters*. Essentially one wishes to know the equilibrium value of an internal coordinate as well as the energy required to displace it from this equilibrium value. Obtaining MM parameters is dealt with in the following two subsections. Subsequent subsections address MM parameter transferability, and other thorny problems in MM modeling of metal complexes.

a Metric parameters

Metric parameters can be obtained from a variety of experimental sources including solid-state neutron and X-ray diffraction, or gas-phase electron diffraction. Alternatively, they can be obtained from high-level *ab initio* quantum calculations on suitable model compounds. If the past decade of quantum chemistry research has proven anything it is this: with the right computational method (the description of which occupies a large literature), one can accurately predict geometries. I qualify 'accurately' since its definition is subjective, but for most purposes this involves theory–experiment agreement of the order of ±0.01 Å for bond lengths and ±1° for bond angles. Torsional (or dihedral) angles are the softest internal modes and hence one's vision of an accurately determined torsional angle depends on the problem at hand. Orpen's research[16] on the systematic analysis of X-ray diffraction structures suggests that the aforementioned guidelines may actually be optimistic given the variability of metal complex geometries with their environment.

b Vibrational parameters

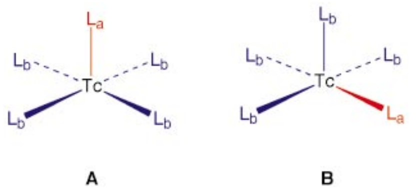
Generally, it is more difficult to obtain vibrational than metric parameters from experiment as force constants must be extracted from spectroscopic, isotopic-labeling studies. Vibrational parameters can be determined from a QM-derived energy Hessian (second derivative of the energy with respect to atomic coordinates).[17] The main sticking point of the QM approach is that for the sake of tractability most vibrational frequencies (and force constants derived from them) are calculated within the harmonic approximation. The reality is that anharmonic effects occur in vibrational spectra, and that experimentally quantifying them is often difficult. This dilemma was largely resolved by a crucial contribution from the Pople group.[17] They showed that QM-calculated, harmonic frequencies generally differ from experimental (and hence anharmonic) frequencies by a constant or scale factor. It is often observed that calculated harmonic frequencies are ≈10% too high. The magnitude of the scale factor changes as one goes to different levels of theory, but the relationship holds up remarkably well.

Recent work by Cundari and Raby[18] has sought to evaluate scaling approximations for estimating MM vibrational parameters for TM complexes. The big stumbling block, as it always seems to be in computational metal chemistry, is the lack of a large and diverse database of reliable experimental results against which one can 'calibrate' the theory. However, our work, as well as that of others, suggests that for a variety of metal systems the approximations first forwarded by Pople and co-workers seem to hold for metal complexes, particularly over a series of related complexes.[17]

c What is a typical gadolinium–nitrogen bond? The transferability issue

Assuming one can obtain metric and vibrational parameters by experiment or calculation, the would-be modeler of metal complexes must deal with transferability. The relatively narrow range of atom and bond types in main group compounds, particularly those involving lighter elements, means that transferability is much less problematic in molecular modeling of organic molecules. The question in this subsection title marks the moment at which this thorny issue impressed itself upon my research group. If we return to the simple ball-and-spring analogy, MM requires the chemist to specify the nature of the balls as well as the springs that connect them. This is a problem as metals often come in a bewildering array of oxidation states [is the Gd–N bond in a gadolinium(III) co-ordination complex a reasonable facsimile of that in a gadolinium(0) organometallic?], bond types (*e.g.* the Gd–N bond involving an amine *versus* an imine ligand), co-ordination numbers, spin states, and co-ordination types. If we further consider the Gd–N bond one must distinguish a Gd–N linkage in a nine-co-ordinate tricapped trigonal prismatic *TRPS*-9) complex from that in a capped square antiprismatic complex, and also among Gd–N bonds involving capping and prismatic co-ordination sites.[19]

Two major approaches have been developed to deal with transferability: ignore it or develop atom/bond types in greater number and with more specificity. The former is more popular. The latter approach involves developing parameters for specific chemical environments, *e.g.* distinguish between the apical (Tc–L$_a$) bond in a square pyramidal TcL$_5$ complex from the four basal (Tc–L$_b$) bonds by giving each set of bonds different q_0 and k, see equation (2) and Scheme 3. Advantages and disadvantages of this approach are obvious. One gains the potential for greater accuracy, but there is a great increase in the number of parameters. Less obvious is the loss of generality



Scheme 3

resulting from a specific MM model. Using the square pyramidal TcL_5 example, one would have to energetically distinguish two isomers (**A** and **B** in Scheme 3) and correctly predict **A** as the more stable candidate. Clearly, as the number (and variety) of ligands increases the situation becomes considerably more problematic.

An interesting approach to transferability in MM was employed by Hay[20] in his work on lanthanide (Ln) aqua and nitrate complexes. It is found, particularly for nine-co-ordinate *TRPS*-9 complexes, that Ln–L bond lengths can differ quite substantially depending on whether the ligand L occupies a capping or prismatic co-ordination site. Prismatic ligands occupy more hindered positions than capping ligands and as a result they typically have longer q_0 for comparable metal–ligand bond types. Given the weakness (*i.e.* low force constant) of gadolinium–ligand bonds, the equilibrium bond lengths can cover a range of 0.1 Å within a single complex. Hay's approach involves the use of very small Gd–L force constants ($k \approx 0.1$ mdyn Å^{-1}; dyn $= 10^{-5}$ N), allowing in essence the bonds to expand or contract in response to steric pressure resulting from non-bonded terms [U_{vdw} in equation (1)]. Although this approach must be employed judiciously, and the results evaluated critically, Hay has shown this to be an efficient and effective technique. Our group followed the lead of Hay for a variety of other co-ordinating atom types for high co-ordination number gadolinium(III) complexes.[19] It is unclear how this simple technique could be applied to transition metal complexes, which have a larger covalent contribution to their bonding than the lanthanides, although research to address this question would be of interest.

d Using organic force fields for inorganic complexes

The majority of efforts at developing MM force fields for metals amount to extending popular 'organic' force fields such as MM2 and AMBER by inclusion of new atom types and parameters. The MM parameters can be divided up into two groups, metal-dependent and metal-independent. It is generally assumed that the metal-independent MM parameters needed to describe an organic ligand are the same whether it is co-ordinated to a metal or not. In other words the N_{amine}–C_{alkane} bond in an edta complex of Gd^{III} has the same force constant and equilibrium bond length whether or not it is co-ordinated to a metal. Chemical intuition suggests that such an approximation is more plausible for co-ordination complexes with their dative/ionic metal–ligand interactions as compared to organometallics which generally have more covalent bonding. A recent contribution from the Comba group[21] has looked at this issue for co-ordination complexes and found that in some cases the use of 'organic' MM parameters for co-ordinated ligands can lead to significant errors. However, the majority of studies on MM modeling of metal complexes have successfully utilized 'organic' force fields for metal-independent parameters.[5–7]

e Parameterizing using static structures

Another sticky issue involves the use of static structures (obtained principally by solid-state crystallography) to assess the predictive ability of a newly developed force field. This issue is not unique to MM modeling of metal complexes. Everyone who has given seminars on MM modeling has almost surely heard the question how do you know the solid-state structure is the same as the solution structure? Answers to this question can range from unimaginative (how do you know it's not?) to metaphysical (what do we mean by molecular structure anyway?). As the field of MM modeling of metal complexes matures it is increasingly desirable to carry out comparisons not only between single complexes, but ensembles of molecules to develop a statistical profile of calculated and experimental metric properties for chemical moieties (*e.g.* $Gd_{\text{CN}=9}$–N_{amine} bonds or N–C–C–N torsional angles in transition metal ethylenediamine complexes, Fig. 1). The wider availability of powerful, easy-to-use graphical packages for mining structural databases will assist in this task. As Orpen[16] points out in his review, by studying the structural variability of a chemical moiety in a variety of solid-state environments one is in some sense modeling the different chemical environments seen in solution. A very narrow range of values for a particular metric parameter in different crystal environments leads one to expect this parameter to be relatively unchanged upon going from the solid to solution phase.

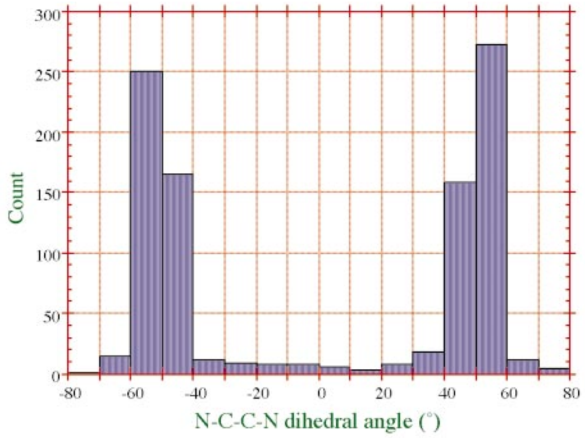
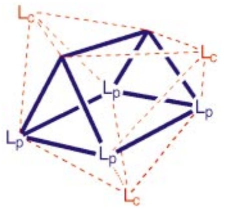


Fig. 1 Histogram showing the range of N–C–C–N dihedral angles in d-block complexes[10]



Scheme 4

f Large co-ordination numbers

A major challenge in MM studies of metal complexes concerns modeling the angular arrangement of ligands about high co-ordination number (CN) metals. Organic molecules tend to have co-ordination geometries that cover a narrow range of angular orientations: it takes a lot of energy and steric pressure to significantly displace an sp^3 C from tetrahedral or to induce non-planarity about the C_{sp^2}=C_{sp^2} double bond of an olefin. Metals, particularly those of the d and f block, generally have a wider range of co-ordination geometries. The situation is particularly troublesome for co-ordination numbers of seven and higher (the norm in f-block chemistry) where there are often minuscule thermodynamic differences and small kinetic barriers among structural polytopes. Also, high CN complexes often have symmetry inequivalent co-ordination sites. Consider a simple homoleptic ML_9, Scheme 4, with *TRPS*-9 geometry. There are two distinct ligand co-ordination sites (capped, L_c, and prismatic, L_p) and six unique L–M–L bond angle types with equilibrium values ranging from ≈70 to ≈140° for a system with an idealized *TRPS*-9 (D_{3h}) structure. Clearly, as one goes to larger co-ordination numbers and different ligating atom types the treatment of the angular interactions about high CN metals becomes increasingly difficult.

One approach to dealing with the challenge of high co-ordination number complexes has its genesis in the work of Kepert.[9] Kepert developed and extensively applied a points-on-a-sphere (POS) model to investigate the stereochemistry of co-ordination complexes. This simple and intuitive (and therefore powerful) model predicts the stereochemistry of metal complexes on the basis of ligand–ligand repulsions (1,3-non-bonding interactions). Conceptually, the method can be thought of as an extension to metal co-ordination complexes of the well known VSEPR model. The lowest energy co-ordination geometry is determined from minimization of a simple functional of the type in equation (3) where r is the

$$V \propto r_{ij}^{-n} \tag{3}$$

distance between ligating atoms i and j, and n is an integer that can range from 1 (Coulombic) to infinity (hard sphere approximation). A value of n in the range of 6 seems to give the closest correspondence with experiment. In the simplest POS implementation ligating atoms are constrained to move on the surface of a sphere centered at the metal atom thereby fixing the metal-ligand distance.

The POS approximation is expected to be most valid in situations in which the metal–ligand bond is highly ionic. In such cases there is minimal directionality arising from covalent, orbitally directed interactions and the preferred co-ordination geometry results from minimization of ligand–ligand repulsions within the constraints of chelation, the stereochemical requirements of the organic ligands, *etc*. Hence, lanthanide complexes are an ideal family of metal complexes for investigation with MM techniques that employ POS approximation. An MM implementation of the POS model to high co-ordination number complexes is well demonstrated by Hay's work on lanthanide aqua and nitrate complexes.[20] An extension of Hay's approach to lanthanide Schiff base and related complexes was reported by Cundari *et al.*[19] Based on the descriptive chemistry of the metals one would expect the POS approximation to also be particularly useful for co-ordination complexes of the alkali metals and alkaline earth metals.

6 Summary, Conclusion and Prospectus

The MM techniques have become routine for many families or organic complexes and the exploitation of this computationally efficient, chemically intuitive model for metal chemistry has attracted increased interest. This contribution has sought to outline some of the current challenges and opportunities in molecular mechanics modeling of metal complexes. Much of the preceding discussion is colored by experience in the author's own lab.[19,22–29] Alternative and complementary views can be found in the growing literature dedicated to molecular mechanics calculations on metal complexes.[5–7]

A combination of quantum calculations and structural databases seems an effective solution to obtaining needed metric and vibrational parameters. Likewise, taking parameters originally derived for organic molecules and using them for the metal-independent parameters of ligands seems to generally be successful although the caveat of Comba and co-workers[21] must always be kept in mind.

From the author's perspective the two immediate, major challenges in MM modeling of metal complexes involve treating L−M−L angular interactions and parameter transferability. The points-on-a-sphere approach is successful for a wide range of metal complexes. In the author's lab MM force fields have been developed using the POS approximation to describe complexes of gadolinium,[19] platinum,[22–23] vanadium,[24,25] chromium[28] and technetium.[29] The greater degree of ionic/dative metal–ligand bonding of metals in the first transition series as compared to second and third row congeners suggests the former will be more amenable to the POS description as will lanthanide complexes *versus* actinide analogues and co-ordination complexes *versus* organometallics. Systematic research on these issues will be of interest from the viewpoint of the important applications of the metals involved, and may yield important new insight into the bonding and structure of metal complexes. Landis *et al.*[30] have developed an alternative method for treating L−M−L bond angles using a valence bond-type approach that designates a hybridization at the metal; preliminary applications to metal alkyl and metal hydride complexes are encouraging and further application of this approach will be of great interest.

In the final scheme of things, the chemist must assess what level of accuracy is required for a particular application in order to select a suitable computational model. I have found in my research on metal complexes that one can carry out reliable (with respect to the tertiary structure of both the metals and ligands) MM conformational searches. This is in large part due to the fact that the preference for a particular conformer is often not inordinately influenced by reasonable uncertainty in the estimation of a few metal-dependent MM parameters. One advantage to a simple MM force field like that in equation (1) is that often these are quite robust with respect to small modifications in the vibrational and metric parameters. Furthermore, the structural similarity of low energy conformations suggests that errors due to neglect of transferability will cancel out to a fair degree.

Two final comments are germane. First, the highly variable nature of bonding in metal complexes, particular TM complexes, that leads to the transferability problem in MM also makes QM modeling of metal complexes challenging. Secondly, of great interest are combined MM/QM methodologies such as outlined by Maseras and Morokuma[31] in which QM methods are used to model metal–ligand interactions (where transferability is probably most significant) while MM is used to describe the main group ligands. Alternatively, it is possible to use MM to perform a quick conformational analysis and obtain low-energy conformations which could then be submitted to further refinement in a separate quantum mechanical step.[24,25,29] Another technique for the inclusion of electronic (and hence quantum) effects such as Jahn–Teller distortions into MM calculations has been addressed by Deeth and Paget.[32] These researchers have added another term to equation (1), the so-called cellular ligand field stabilization energy (CLFSE), to model stereochemical effects arising from the variable occupancy of the d orbital manifold.

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