Molecular Mechanics for Coordination Complexes: The Impact of Adding d-Electron Stabilization Energies

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Abstract: An electronic energy term for transition metals has been constructed for extending Molecular Mechanics (MM) to open-shell, Werner-type coordination compounds. The d-orbital energies from a generalized ligand field calculation are used to compute the Cellular Ligand Field Stabilization Energy (CLFSE). The CLFSE models the geometrical effects of the stereochemical activity of d electrons and can be computed for any coordination number, molecular symmetry, and ligand type. In conjunction with ligand-ligand nonbonding and metal-ligand bond stretch terms, CLFSEs provide a general framework for incorporating transition metals into MM. An explicit angle-bend term is not required. After describing the theoretical basis of CLFSEs, the method is illustrated using a range of six-coordinate high-spin and four-coordinate low-spin Ni^{II} amine complexes plus four-, five- and six-coordinate Cu^{II} amine systems. For the nickel complexes, the spin-state change is modeled simply by changing the d-orbital occupancies. A single set of force field and CLF parameters simultaneously reproduces the metal coordination for all ten nickel complexes with overall root-mean-square errors of 0.010 Å in Ni-N bond lengths and 0.621° in N-Ni-N angles. For the copper compounds, the (slightly modified) force field *automatically* models the Jahn-Teller distorted structures of six-coordinate species, the planar coordination in the four-coordinate compounds, and the distorted geometries of five-coordinate systems. The root-mean-square errors in bond lengths and angles for all 15 Cu molecules are higher (0.024 Å and 0.897°, respectively) due to the inherent variability of the structural data. Copper complexes, especially pentacoordinate ones, are intrinsically flexible or "plastic" which, with the added influence of the Jahn-Teller effect, can result in large geometrical changes from relatively minor crystal packing effects.

Introduction

Molecular Mechanics (MM) is a popular method for modeling molecular structure and conformational energies[1] with well-parametrized force fields available for treating many essentially "organic" problems in chemistry and biochemistry.[2-6] However, the extension of MM to inorganic chemistry and especially to Transition-Metal (TM) systems presents greater challenges.[7-13]

One of the main difficulties with conventional MM treatments of metal systems is the treatment of high coordination numbers[7,13] and the definition of valence angle-bend terms. For example, *cis* and *trans* L-M-L combinations in octahedral symmetry must be handled differently. Many workers have now overcome this so-called "unique labeling" problem. A particularly elegant solution is based on spherical coordinates.[7]

Various metal species have been tackled ranging from classical Werner coordination and macrocyclic complexes[7-10,13] through metalloporphyrins[11] to organometallic systems.[12] However, all these methods only tackle part of the problem. None has yet provided a general method for treating the additional effects arising from electronic terms. In Werner complexes, the electronic effects of an open d shell can lead to severe

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geometrical distortions which are well-known in coordination chemistry.[14] Of special note are the distorted non-cubic geometries displayed by the majority of d^9 Cu^{II} complexes. Six-coordinate Cu^{II} species, for example, are virtually always tetragonally elongated. Other geometries like those for planar low-spin d^8 species can be seen as the consequence of a Jahn−Teller distortion of the excited ^1E state of the parent octahedral system.[15] Current MM formalisms would be obliged for a CuL_6 species, for example, to define different parameter sets for different metal−ligand bond lengths even though L might be identical in both cases. In more complicated mixed-ligand systems, one would have to decide *a priori* which parameter set to apply to which ligand and this may not be desirable or obvious.

Many distortions of coordination complexes can be rationalized in terms of the Jahn−Teller effect or, equivalently, in terms of the Ligand Field Stabilization Energy (LFSE).[15] The LFSE is a more general concept and applies beyond orbitally degenerate Jahn−Teller active systems like octahedral d^9 Cu^{II} complexes. For example, the detailed variation of M−L distances in a series of first-row metal complexes such as $[M(saccharide)_2(H_2O)_4]^{2+}$ [16] and $[M(Me_6tren)Br]^+$ [17] can be traced to the underlying arrangement of the d electrons. It appears necessary, therefore, that a general MM treatment of open-shell TM systems should include explicitly in the strain energy expression some kind of Ligand Field Stabilization Energy term to account for this "stereochemical activity" [17] of d electrons.

This paper describes such an energy term and our first applications. (We presented a preliminary account at the International Conference on Bioinorganic Chemistry, Oxford, UK, 1991.[18]) The method is based on a combination of conventional Molecular Mechanics and Cellular Ligand Field (CLF) model of Gerloch and Woolley.[19] The so-called Cellular Ligand Field Stabilization Energy (CLFSE) has several important and novel features. Not only does it provide a metal-centered term which automatically models the geometrical consequences of the electronic stabilization energy of an incomplete d shell but the CLFSE is also independent of any assumptions concerning coordination number, geometry, and ligand type.

The CLFSE/MM method can do more than mimic existing conventional force fields for open-shell Werner-type coordination compounds. As illustrative examples, we consider the problem of high- and low-spin Ni^{II} amine complexes and the treatment of Jahn−Teller effects and the geometries in Cu^{II} amine systems. Independent conventional force fields exist for each Ni case[8] yet, from a CLFSE viewpoint, the only relevant difference is the d-orbital occupations. Using the same FF and CLF parameters but with d-orbital populations that reflect the desired spin state, the CLFSE/MM method accurately reproduces the structures of a range of complexes. That is, essentially the same FF can model quite different geometries and Ni−N interactions. Conventional approaches have also been suggested for Cu^{II} species[10,13,20] but can only be applied to limited sets mainly of four-coordinate molecules. Attempts to treat six-coordinate species require external constraints to force the molecule along a tetragonal distortion.[15] In contrast, the CLFSE/MM approach uses a single FF to compute the structures of four-, five-, and six-coordinate complexes to good accuracy. Of particular importance is that the Jahn−Teller distortion of six-coordinate Cu^{II} is automatically accounted for.

Theoretical Basis

The general form for the extended CLFSE/MM strain energy, E_{tot}, is

$$E_{tot} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + \mathrm{CLFSE} \qquad (1)$$

The terms in eq 1 refer respectively to bond stretch, angle bend, torsional, nonbonding, and CLFSE interactions, respectively. Each complex can be divided into a metal-based part and a ligand-based part. The former comprises the metal and the atoms bound to it, while the latter comprises the ligand groups. The M−N−L angles span both parts.

The CLFSE and its derivatives are only computed for displacements of the ligand atoms. This is reasonable for simple σ-bonding amines which behave as monatomic ligands. Modifications to include displacements of the second coordination shell (i.e. the atoms connected to the ligand donors) are being developed for unsaturated, π-bonding ligands and will be reported in due course.

The coordination geometry is specified by the M−L distances and the L−M−L angles. The bond lengths are treated using a Morse function

$$E_{str} = D_0[1 - e^{-\alpha(r-r_0)}]^2 - D_0 \qquad (2)$$

since some bonds, especially for distorted octahedral Cu complexes, vary dramatically rendering a harmonic expression a poor approximation. Simple repulsion models, such as VSEPR theory[21] and Kepert's approach,[22] show that, in the absence of extra electronic effects, ligand−ligand interactions determine the angular geometry. The CLFSE implicitly contains an L−M−L angle bending contribution. However, the method described here should be general and there are certain d configurations which have a zero CLFSE (e.g. high-spin d^5). Such cases require an additional term to model the bond angles. One could use conventional MM methodology with explicit angle bend terms but, as mentioned above, this approach has its difficulties. Instead, the whole unique labeling problem[7] can be avoided by using 1,3 (i.e. ligand−ligand) nonbonded interactions (eq 3). A similar approach has been adopted by Comba.[20]

$$E_{vdw} = A/r^9 - B/r^6 \qquad (3)$$

Hence, the CLFSE/MM model requires three terms for the metal part of the force field: (i) the CLFSE, (ii) M−L Morse functions for bond stretching, E_{str} (eq 1), and (iii) atomic nonbonding terms, E_{vdw}, for ligand−ligand interactions (eq 2). The remainder of the molecule is treated in a conventional way. The bending and torsional terms employ the normal harmonic and cosine functions respectively with certain parameters involving the metal atom set to zero (see Table 4 for a full listing of the FF). Apart from the 1,3 ligand−ligand terms, Van der Waals interactions are only considered for atom pairs separated by more than three bonds. In common with other workers,[7,8,11-13,20] we have not yet included electrostatic interactions in the model.

A hybrid CLFSE/MM program package DOMMINO (**D-O**rbitals in Molecular **M**echanics of **INO**rganics) has been developed by adding routines for computing the CLFSE and its derivatives to in-house MM software.[23] The modifications to the total energy and derivative calculations are straightforward since the CLFSE part is virtually self-contained. A simple interface to the SYBYL molecular modeling

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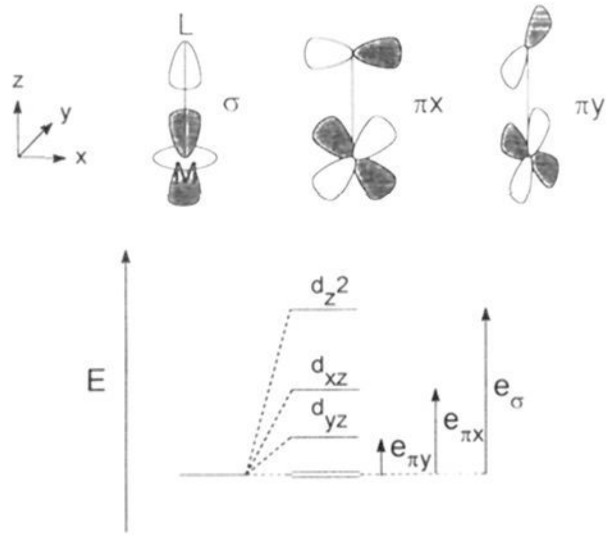

Figure 1. Schematic representations of the symmetry interactions between the d orbitals local to a given cell and appropriate bonding functions. The resulting changes in the d-orbital energies are displayed as functions of the CLF parameters e_σ, $e_{\pi x}$, and $e_{\pi y}$.

package[24] has been constructed for inputting structures to DOMMINO and analyzing the results.

The CLFSE Term. To implement CLFSEs one must compute derivatives with respect to atomic displacements. For "normal" MM energy terms, a simple function is employed which has analytical derivatives. An analytical derivative of the CLFSE term cannot be constructed since the CLFSE is computed from the d-orbital energies of the underlying CLF calculation[19,25] and this requires a 5 × 5 diagonalization.

In the CLF model, the potential surrounding the metal ion is notionally divided into spatially discrete regions or cells where each cell normally contains a single metal–ligand bond. The ligand field perturbation in each cell can then be divided into separate σ and π components which are expressed in terms of the energy parameters e_σ, $e_{\pi x}$, $e_{\pi y}$ as shown schematically in Figure 1. These parameters are defined relative to the local M–L coordinate frame. The global ligand field potential, V_{LF}, is then constructed by summing all the local contributions together, taking due note of the relationship between the local and global axis frame definitions as described by Gerloch.[25]

The advantages of the CLF model are that (i) the symmetry of the ligand field is implicit in the ligand coordinates and (ii) the CLF e_λ parameters ($\lambda = \sigma, \pi x$, and πy) refer to individual M–L interactions. The CLFSEs are therefore general and can handle any ligand type and coordination environment. This paper deals only with saturated amines which are the simplest ligand type requiring a single CLF parameter, e_σ. The extension to π-bonding ligands is straightforward and will be the subject of future publications.

The mathematics of CLF theory is conveniently handled via tensor operator theory whereupon the d-orbital matrix elements become:

$$\langle d_i|V_{LF}|d_j\rangle = \sum_{l}^{\text{cells}} \sum_{k}^{\text{modes}} \mathbf{T}^{l*}_{ik}\,\mathbf{T}^{l}_{kj}\,e^{l}_{k} \qquad (4)$$

V_{LF} is the ligand field potential between d orbitals i and j and the $\mathbf{T}_{ik}$ are unitary matrices defining the relationships between local and global axis frames. Diagonalization of the ensuing 5 × 5 matrix yields the d-orbital energies, $\epsilon(d_i)$, from which the CLFSE is computed simply as:

$$\text{CLFSE} = \sum_{i=1}^{n} \varrho(d_i)\epsilon(d_i) \qquad (5)$$

Here, $\varrho(d_i)$ are the d-orbital occupations (normally 0, 1, or 2). Note that we adopt a one-electron $|1sm_lm_s\rangle$ coupling scheme as employed in Master Equation M.2 of ref 25 (p 371) rather than the more general many-electron $|LSJM_J\rangle$ scheme of Master Equation M.3. The CLFSE is therefore a strictly one-electron term with d-orbital energies that are automatically barycentered. Different d configurations and spin states can then be simulated simply by changing the d-orbital occupancies. Implicit in such a treatment is the assumption that the spin state and d configuration are well-defined. These restrictions presumably preclude application of CLFSEs to organometallic systems although, fortunately, it appears that such species are amenable to more conventional MM approaches.[9]

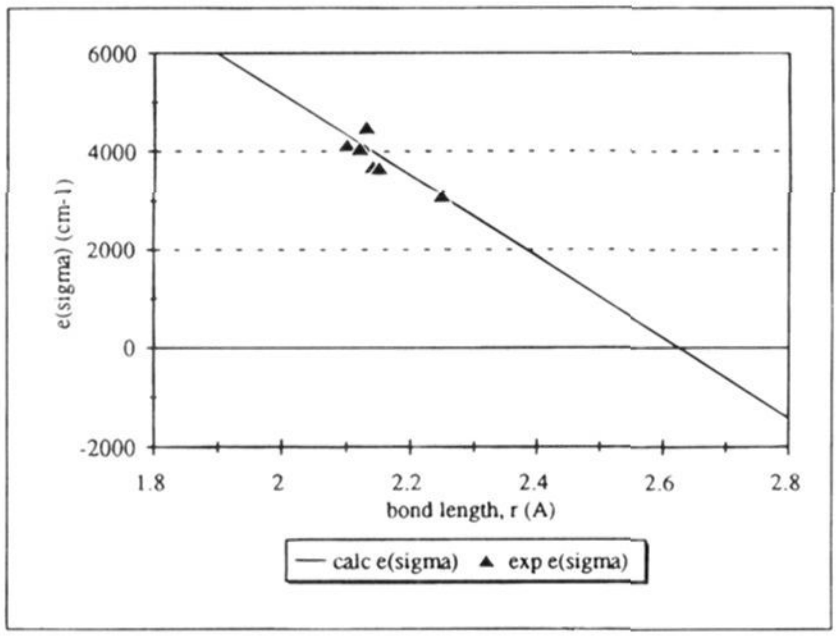

Figure 2. Graph showing the relationship between e_σ values for Ni–N(amine) bonds calculated using eq 6 (solid line) and empirically observed values from ref 27 (triangles).

The diagonalization of V_{LF} precludes any simple analytical expression for the CLFSE and its derivative. This represents the major difference between our approach and conventional MM. However, our experience to date indicates that numerical finite-difference derivatives are adequate. It is then straightforward to insert the CLFSE code into the MM program at the points where derivatives and total strain energies are computed. The CLFSE/MM method described here is thus a complete generalization of the simple formulas derived by Deeth and Hitchman[15] for treating tetragonal geometries in d^9 and d^8 species.

For many systems, the diagonalization will not exact an undue penalty in computation time. The CLFSE contribution is not evaluated for all atomic displacements, only those relevant to the M–L coordination. In a large metalloenzyme with only a few metal centers, for example, the calculation would only be slightly slower than for a comparable "all-organic" system.

The CLFSE requires an expression relating the M–L bond length to the CLF parameter value. Both simple theory and experiment suggest for octahedral complexes that the ligand field splitting parameter 10*Dq* or Δ_{oct} should have an approximately $1/r^5$ dependence on the metal–ligand bond distance, r.[15,26] For simple σ-bonding-only ligands like amines, $\Delta_{oct} = 3e_\sigma$ implying that the CLF parameter should also display a $1/r^5$ dependence.

For the particular case of high-spin Ni^{II} complexes, however, it has been shown[27] that e_σ varies linearly with Ni–N distance at least over the range of about 2.0 to 2.3 Å. Accordingly, the expression for e_σ as a function of Ni–N bond length, r, is

$$e_\sigma = 21629 - 8235r \qquad (6)$$

The fit between empirical e_σ values and this straight line is shown in Figure 2.

Having chosen a functional form for e_σ, the remaining parameters of the M–N bond stretch were determined by fitting the Morse function plus CLFSE for a hypothetical Ni–N diatomic to the harmonic functions reported for high- and low-spin Ni^{II}–N.[8] For a hypothetical octahedral high-spin d^8 NiN_6 complex, the CLFSE is $-6/5\Delta_{oct}$ or $-18/5e_\sigma$ while for a hypothetical low-spin d^8 NiN_4 system it is $-22/5e_\sigma$. Dividing through by six and four respectively, the relevant CLFSEs for high- and low-spin diatomic systems are $-0.6e_\sigma$ and $-1.1e_\sigma$. A process of trial and error then established the remaining Morse function

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[24] The SYBYL Molecular Modelling package, Version 6.1, is available from TRIPOS Associates: 1699 South Hanley Road, Suite 303, St. Louis, Missouri 63144.

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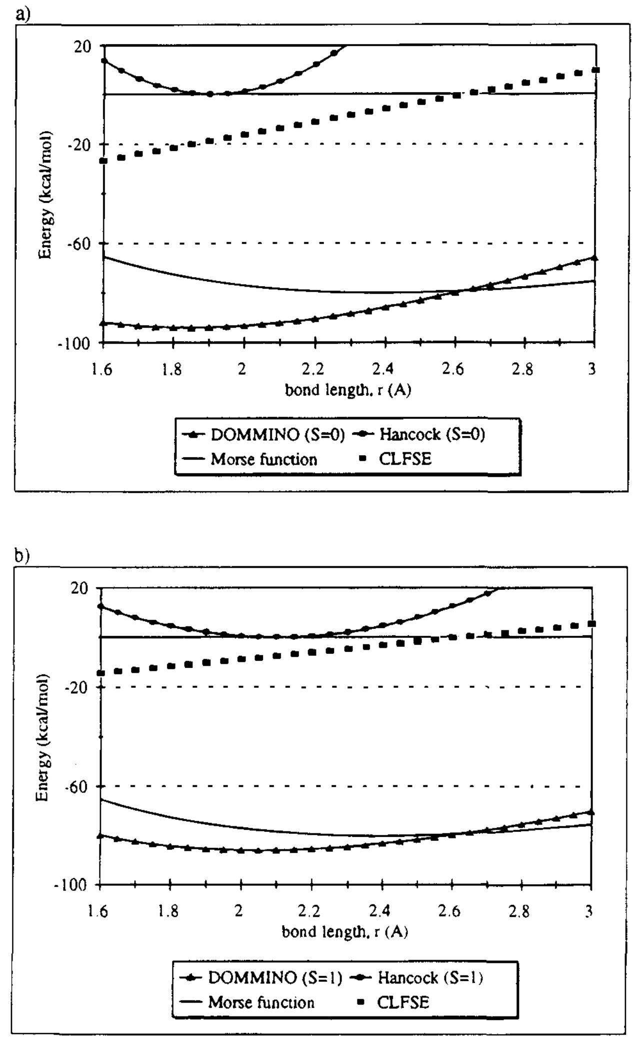

Figure 3. Comparison of bond stretch strain energy curves for the harmonic functions reported by Hancock[8] (circles) and the CLFSE plus Morse functions used in DOMMINO (triangles). The separate contributions of the CLFSE (squares) and the Morse function (solid curved line) are also displayed. (a) High-spin Ni^{II}, $S = 1$; (b) low-spin Ni^{II}, $S = 0$.

parameters of $r_0 = 2.393$ Å, $D_0 = 80.0$ kcal/mol, and $\alpha = 0.45$ as capable of approximately reproducing both high- and low-spin harmonic potential curves in the vicinity of the relevant minima. The requirement of a single FF capable of treating both spin states simultaneously results in slight displacements of the CLFSE/MM curves relative to the harmonic functions. A comparison of these various curves is given in Figure 3.

For Cu, the only changes are a modified r_0 value of 2.283 Å and a Cu−N−C angular potential with $k_\theta = 14.39$ kcal/mol and $\theta_0 = 124°$ (see Table 4). We recognize that the use of a linear function for the e_σ values of copper complexes is a relatively poor approximation to the empirically observed variation.[26] However, our aim here is to reproduce structures so that the actual values of the CLF parameters are irrelevant. Should we wish subsequently to compute d−d transition energies, we can always adopt the procedures introduced by Comba,[20] who employs the Angular Overlap Model (AOM) to calculate various ligand field quantities (d−d spectra, electron spin resonance g values) after first determining the structure using more or less conventional MM. Given the same e_λ parameter sets and molecular geometries, the AOM and the CLF model produce identical results.

For both metals, the r_0 values are larger than the normally anticipated M−L distances. (See Figure 3.) This is a general feature of the CLFSE/MM method. The CLFSE becomes increasingly negative as the bond lengths decreases. The balance between the CLFSE, which gives a (discontinuous) minimum for a zero bond length, and the Morse function, which minimizes at r_0, tends to be a computed bond distance somewhat less than r_0.

Results and Discussion

Twenty-three amine complexes with saturated hydrocarbon backbones and two hexaammine species have been located comprising six octahedral high-spin and four planar low-spin Ni^{II} species plus five six-coordinate, seven four-coordinate, and three five-coordinate Cu^{II} compounds. All the structures (except for the $[M(NH_3)_6]^{2+}$ species) were obtained from the Cambridge Structural Database[28] and are displayed schematically in Figure 4 and listed in Table 1.

Nickel Complexes. The average observed and calculated bond lengths and angles for the ten Ni^{II} complexes are given in Table 2 and, where possible, compared with the results from the conventional MM treatment of Hancock.[8] Individual and average root-mean-square (rms) errors for these parameters calculated over the individual bond lengths and angles are given in the supplementary information. (A complete listing of all the FF parameter values is included in Table 4.)

Overall, the performance of the CLFSE/MM method with respect to the metal coordination environment is at least as good as conventional MM. The average rms errors in bond lengths and bond angles are only 0.010 Å and 0.62°, respectively. For individual complexes, the computed Ni−N distances are generally within three times the average rms error. The worst agreement is for $[Ni(dptn)_2]^{2+}$ (**V**) where the average Ni−N rms error is 0.021 and the computed bond lengths are systematically too short by up to 0.08 Å.

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Table 1. Chemical Formulas, Full Ligand Names, Coordination Numbers, and Cambridge Structural Database Reference Codes for the Molecules Shown in Figure 1

no.	formula	coord no.	ligand name	CSD refcode	ref
I	$[Ni(NH_3)_6]^{2+}$	6			29
II	$[Ni(en)_3]^{2+}$	6	ethylenediamine	ENIACH	30
III	$[Ni(tn)_3]^{2+}$	6	1,3-diaminopropane	DAMPNI	31
IV	$[Ni(dien)_2]^{2+}$	6	diethylenetriamine	AEAMNI10	32
V	$[Ni(dptn)_2]^{2+}$	6	bis(3-aminopropyl)amine	AMPRNI10	33
VI	$[Ni(tcn)_2]^{2+}$	6	1,4,7-triazacyclononane	BAZNNI	34
VII	$[Ni(en)_2]^{2+}$	4	ethylenediamine	EANBAG01	35
VIII	$[Ni(tmc)]^{2+}$	4	tetra-*N*-methylcyclam	DITMUO	36
IX	$[Ni(meso14ane)]^{2+}$	4	[7*R*(*S*),14*S*(*R*)]-5,5,7,12,12,13-hexamethyl-1,4,8,11-tetraazacyclotetradecane	MAZNIA	37
X	$[Ni(B\text{-}12\text{-}aneN_4)]^{2+}$	4	1,4,7,10-tetraazabicyclo[8.2.2]tetradecane	GALZUO	38
XI	$[Cu(NH_3)_6]^{2+}$	6			39
XII	$[Cu(en)_3]^{2+}$	6	ethylenediamine	CUENCL	40
XIII	$[Cu(tcn)_2]^{2+}$	6	1,4,7-triazacyclononane	DUSJAC01	41
XIV	$[Cu(dien)_2]^{2+}$	6	diethylenetriamine	ETACUB	42
XV	$[Cu(tach)_2]^{2+}$	6	triaminocyclohexane	TACCUP	43
XVI	$[Cu(papd)]^{2+}$	5	2,5,8,11,14-pentaazapentadecane	LATSII	46
XVII	$[Cu(apt)]^{2+}$	5	1,4-bis(3-aminopropyl)-1,4,7-triazacyclononane	JIBZUP	44
XVIII	$[Cu(adt)]^{2+}$	5	*N,N*-bis(2-aminoethyl)diethylenetriamine	TENCUB	45
XIX	$[Cu(en)_2]^{2+}$	4	ethylenediamine	CEDHAU	47
XX	$[Cu(tn)_2]^{2+}$	4	1,3-diaminopropane	DAPRCU	48
XXI	$[Cu(dmed)_2]^{2+}$	4	(dimethylamino)ethyl)amine	DMEDCU	49
XXII	$[Cu(med)_2]^{2+}$	4	*N*-methylethylenediamine	CMENOX	50
XXIII	$[Cu(nen)_2]^{2+}$	4	*N*-ethylethylenediamine	ETEACU	51
XXIV	$[Cu(deen)_2]^{2+}$	4	*N,N*-diethylethylenediamine	CEFBEU	52
XXV	$[Cu(chn)_2]^{2+}$	4	1,3-diaminocyclohexane	CHXCUA	53

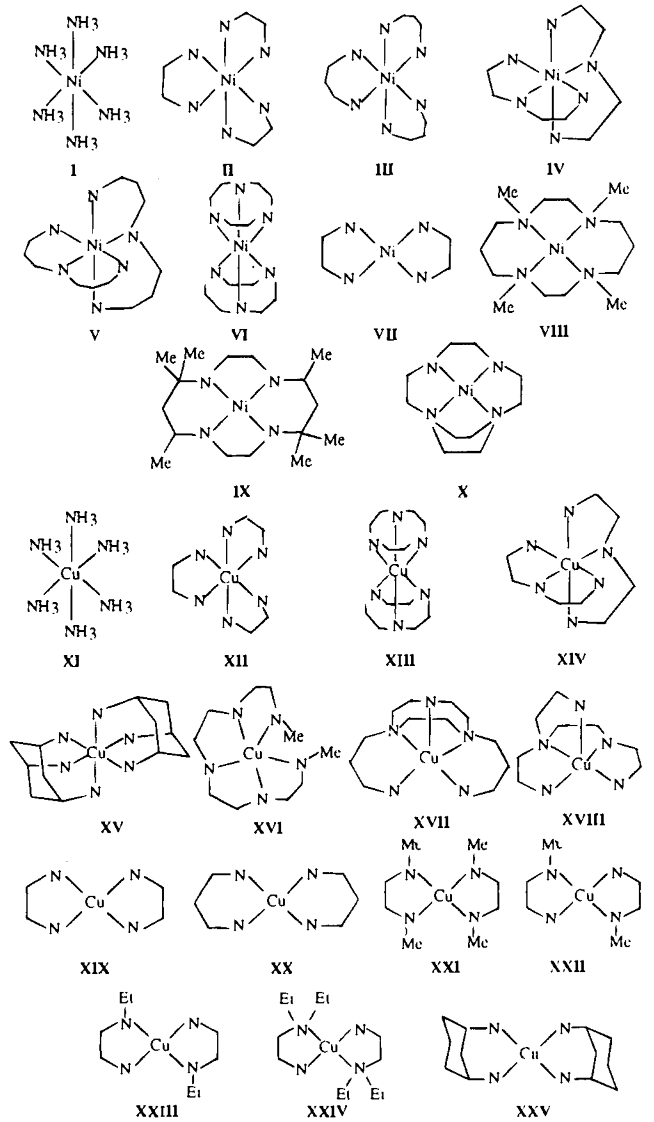

Figure 4. Schematic diagrams of the amine complexes used in this study. See Table 1 for more details.

A significant feature of the CLFSE/MM approach is that the coordination geometry is implicit in the CLFSE. Hence, for high-spin d^8 NiN_6, the CLFSE maximizes for octahedral symmetry while for low-spin d^8 NiN_4, the maximum CLFSE is for a planar geometry. This contrasts with conventional MM where some form of explicit angle bend or out-of-plane term is required to enforce planar coordination.

An indication of the method's performance for the rest of the molecule was obtained by computing the rms errors for Ni—N—C angles and the remaining "organic" bond lengths and angles (excluding any involving hydrogen) as well as the maximum deviation for the Ni—N—C bonds in each complex. (A full listing is included in the supplementary information.) The latter is generally less than about 7° except for $[Ni(B\text{-}12aneN_4)]^{2+}$ (**X**) where one Ni—N—C angle differs by 13.2° with respect to experiment. As for $[Ni(dptn)_2]^{2+}$, six-membered chelate rings are involved (vide infra). The average rms error for the Ni—N—C angle is 0.87° while the average rms errors for the remaining bond lengths and angles (excluding any involving H) are 0.008 Å and 0.598°, respectively.

Overall, therefore, the agreement with experimental structures for both high- and low-spin Ni^{II} amine complexes is good. There is a sharp division between high-spin octahedral and low-spin planar geometries with around a 0.2 Å shortening of the Ni—N distances for the latter. The achievement of the CLFSE/MM data is that only a *single* set of FF parameters is required in contrast to conventional MM which employs independent FFs for high- and low-spin systems.

These results suggest a possible future application of the CLFSE/MM method for modeling spin crossovers. Providing that the initial and final spin states are well-defined and can be represented in terms of simple one-electron configurations, one could imagine following a spin crossover by progressively mixing the relevant two sets of d-orbital occupations. The crossover region would then be associated with non-integral d-orbital populations.

Another important observation concerns a hypothetical "bare ligand" NiN_6 molecule. It has already been suggested[15] that the planar geometries of low-spin d^8 complexes can notionally

Table 2. Observed and Calculated Bond Lengths (Å) and Angles (°) Describing the Ni Coordination Environment[a]

	$[Ni(NH_3)_6]^{2+}$ (**I**)		$[Ni(en)_3]^{2+}$ (**II**)			$[Ni(tn)_3]^{2+}$ (**III**)			$[Ni(dien)_2]^{2+}$ (**IV**)			$[Ni(dptn)_2]^{2+}$ (**V**)		
	calc	obs[29]	**calc**	obs[30]	*Han*	**calc**	obs[31]	*Han*	**calc**	obs[32]	*Han*	**calc**	obs[33]	*Han*
Ni–N (Å)	**2.12**	2.13	**2.12**	2.13	*2.12*	**2.14**	2.15	*2.15*	**2.05** **2.15**	2.06 2.16	*2.05* *2.16*	**2.15** **2.11**	2.23 2.15	*2.20* *2.11*
average	**90.0**	90.0[a]	**81.8**	81.9	*84.3*	**83.8**	86.9	*85.1*	**81.7**	81.6	*82.9*	**91.6**	90.4	*91.2*
N–Ni–N (°)	**180.0**	180.0[a]	**173.1**	171.8		**173.1**	175.8		**168.0**	167.3		**177.4**	176.4	

	$[Ni(tcn)_2]^{2+}$ (**VI**)			$[Ni(en)_2]^{2+}$ (**VII**)			$[Ni(tmc)]^{2+}$ (**VIII**)			[Ni(meso14ane)]$^{2+}$ (**IX**)			$[Ni(B\text{-}12\text{-}aneN_4)]^{2+}$ (**X**)		
	calc	obs[34]	*Han*	**calc**	obs[35]	*Han*	**calc**	obs[36]	*Han*	**calc**	obs[37]	*Han*	**calc**	obs[38]	*Han*
Ni–N (Å)	**2.11**	2.11	*2.09*	**1.94**	1.92	*1.92*	**1.99**	1.98	*1.97*	**1.98**	1.96		**1.85**	1.87	*1.86*
average	**80.7**	82.6	*82.6*	**87.6**	86.4	*88.5*	**90.3**	90.6	*86.4*	**90.0**	90.0		**89.7**	89.7	
Ni–Ni–N (°)	**177.8**	177.1		**179.7**	180.0	*180.0*	**167.4**	168.6	*166.0*	**180.0**	180.0		**169.8**	169.1	

[a] The experimental values were quoted as average values for the specific bond angles.

be derived from a Jahn–Teller distortion of the ^1E excited state of the octahedral complex. In support of this, a *low-spin* d^8 configuration yields a tetragonally elongated system with $Ni-N_{eq} = 1.90$ and $Ni-N_{ax} = 2.78$ Å relative to a computed Ni–N distance of 2.1 Å for the parent octahedral case.

Copper Complexes. For d^9 copper complexes, the CLFSE/MM approach *automatically* generates the tetragonal geometry for the first-order Jahn–Teller active ^2E_g state. For the "bare ligand" system, the $Cu-N_{eq}$ distance is 1.96 Å and $Cu-N_{ax}$ is 2.45 Å relative to a computed distance of 2.13 Å for a regular octahedron. A contour plot of the total strain energy as a function of equatorial and axial bond lengths is shown in Figure 5. Others have also reproduced such distortions but with external constraints to force the molecule along a particular coordinate.[15,54] In contrast, these distorted geometries arise from the CLFSE and no constraints are required. This is a significant advance in molecular modeling of coordination complexes, especially those of d^9 metals.

Copper(II) is probably the hardest metal ion for conventional MM. Virtually all applications are restricted to four-coordinate species[13] which are generally more straightforward (vide infra). The CLFSE/MM scheme therefore represents the first general method for handling any coordination number and geometry. However, before discussing the results, we must consider the experimental structures to which the computed structures are compared.

Copper(II) complexes are notoriously "plastic".[55] This means that a range of structures are possible which have similar energies and the final "observed" solid-state structure may depend critically on relatively subtle crystal packing forces. As an example, consider trigonal-bipyramidal (TBP) versus square-pyramidal (SQP) coordination.

In TBP symmetry, there is a hole in the d_{z^2} orbital. The resulting "stereochemical activity" [17] of the d-electrons facilitates a closer approach of the axial ligands relative to, say, a comparable d^{10} zinc compound. Thus, the zinc species has longer axial than equatorial bonds while the relative bond lengths in d^9 copper systems are reversed and one observes two short axial contacts and three medium equatorial distances. In contrast, SQP symmetry has the hole in the equatorial $d_{x^2-y^2}$ orbital where the stereochemical activity yields four short equatorial bonds and a quite long apical contact (see Figure 6).

CLFSE/MM calculations illustrate this more quantitatively. For a model TBP "bare ligand" CuN_5, the optimized axial and equatorial distances are 1.88 and 2.28 Å, respectively, compared with the equatorial and apical distances of 2.01 and 2.48 Å for SQP symmetry. The energies are very similar (the C_{4v} system is 2 kcal/mol lower in energy). Experimentally, five-coordinate Cu^{II} frequently display intermediate and variable structures as shown by the $[Cu(2,2'\text{-bipyridyl})_2X]^{n+}$ complexes where Hathaway has mapped out a series of structures from near trigonal bipyramidal through to near square pyramidal.[56]

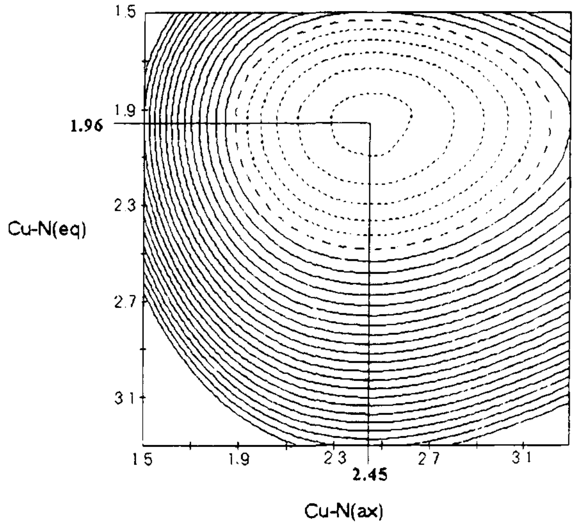

Figure 5. Contour plot of the total strain energy for a hypothetical "bare ligand" CuN_6 complex as a function of the equatorial and axial bond lengths. Successive contours are separated by 1 kcal/mol. Solid lines represent positive energies, long dashes correspond to zero energy, and short dashes indicate negative energies.

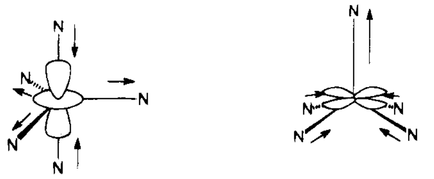

Figure 6. Schematic representation of the stereochemical activity of the singly occupied d orbital in d^9 CuN_5 complexes. The arrows indicate the motions of the ligands relative to a closed-shell d^{10} systems.

Thus, unless the calculations explicitly include the effects of the surrounding lattice, one cannot expect to get exact agreement with the solid state structure of five-coordinate Cu^{II} complexes unless the crystal does not alter the structure from what would be observed in the vacuum phase. Unfortunately, experimental gas phase structures of these cationic copper complexes are not available. One could attempt to verify the CLFSE/MM results

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Table 3. Observed and Calculated Bond Lengths (Å) and Angles (°) Describing the Cu Coordination Environment[a]

	$[Cu(NH_3)_6]^{2+}$ (**XI**)		$[Cu(en)_3]^{2+}$ (**XII**)		$[Cu(tcn)_2]^{2+}$ (**XIII**)		$[Cu(dien)_2]^{2+}$ (**XIV**)		$[Cu(tach)_2]^{2+}$ (**XV**)[b]	
	calc	obs[39]	**calc**	obs[40]	**calc**	obs[41]	**calc**	obs[42]	**calc**	obs[43]
Cu−N (Å)	**2.48**	2.45[c]	**2.44**	2.49	**2.36**	2.34	**2.45**	2.46	**2.29**	2.35
	2.04	2.15[e]	**2.44**	2.33	**2.35**	2.30	**2.42**	2.35	**2.01**	2.07
			2.09	2.11	**2.12**	2.08	**2.04**	2.13		
			2.08	2.09	**2.10**	2.06	**2.07**	2.07		
			2.03	2.06	**2.02**	2.05	**2.14**	2.04		
			2.03	1.91	**2.01**	2.05	**1.98**	2.03		
average N−Cu−N (°)	**90.0**	90.0[d]	**79.1**	80.7	**79.2**	81.3	**80.0**	80.6	**85.2**	87.0
	179.9	180.0[d]	**169.7**	168.9	**177.7**	178.2	**165.3**	166.1		

	$[Cu(papd)]^{2+}$ (**XVI**)		$[Cu(apt)]^{2+}$ (**XVII**)		$[Cu(adt)]^{2+}$ (**XVIII**)	
	calc	obs[46]	**calc**	obs[44]	**calc**	obs[45]
Cu−N (Å)	**2.41**	2.16	**2.33**	2.25	**2.04**	2.04
	2.16	2.09	**1.96**	2.03	**2.14**	2.09
	1.97	2.01	**2.10**	2.08	**2.47**	2.09
	2.01	2.03	**2.03**	2.06	**2.02**	2.01
	2.02	2.02	**2.05**	2.03	**1.97**	2.01
N−Cu−N (°)	**78.6**	84.9	**80.5**	84.0	**110.0**	113.1
	112.7	111.8	**94.1**	105.3	**75.6**	83.2
	109.1	104.9	**102.3**	101.6	**101.4**	116.7
	101.7	108.0	**77.9**	81.5	**112.4**	105.0
	85.7	85.1	**89.9**	90.3	**84.3**	86.1
	170.5	167.8	**171.9**	173.2	**143.1**	128.2
	98.9	99.6	**86.2**	86.3	**99.1**	96.3
	86.1	84.5	**174.7**	172.9	**85.4**	86.4
	145.5	140.2	**92.7**	87.8	**169.2**	169.6
	85.3	84.4	**91.7**	94.9	**85.8**	84.1

	$[Cu(en)_2]^{2+}$ (**XIX**)		$[Cu(tn)_2]^{2+}$ (**XX**)		$[Cu(dmed)_2]^{2+}$ (**XXI**)		$[Cu(med)_2]^{2+}$ (**XXII**)		$[Cu(nen)_2]^{2+}$ (**XXIII**)		$[Cu(deen)_2]^{2+}$ (**XXIV**)		$[Cu(chn)_2]^{2+}$ (**XXV**)	
	calc	obs[47]	**calc**	obs[48]	**calc**	obs[49]	**calc**	obs[50]	**calc**	obs[51]	**calc**	obs[52]	**calc**	obs[53]
average Cu−N (Å)	**2.02**	2.02	**2.00**	2.04	**2.04**	2.06	**2.01**	2.01	**2.02**	2.01	**2.02**	2.01	**2.00**	2.02
							2.04	2.06	**2.03**	2.03	**2.10**	2.08		
average N−Cu−N (°)	**85.4**	84.1	**84.8**	86.7	**86.7**	85.3	**86.3**	85.9	**86.2**	85.0	**85.2**	84.9	**85.5**	87.6
	180.0	180.0	**180.0**	180.0	**177.3**	180.0	**180.0**	180.0	**180.0**	180.0	**180.0**	180.0	**180.0**	180.0

[b] For $[Cu(tach)_2]^{2+}$ a full set of experimental data was not available for the purpose of comparison with calculated values.
[c] The experimental data for this value was quoted with an error of ±0.28.
[d] The experimental data quoted was an average value only.
[e] The experimental data for this value was quoted with an error of ±0.08.

further either by computing gas phase structures using *ab initio* theory or by extending the model to include the crystal lattice effects. Both of these avenues are being explored.

Apart from the "plasticity" of d^9 Cu species, six-coordinate copper complexes are also subject to the Jahn−Teller effect. Hence, not only can quite different structures be observed for essentially the same complex due to plasticity, apparent multiple structures can also result from static or dynamic Jahn−Teller effects where the molecule may occupy more than one minimum on the warped Mexican Hat potential energy surface.[57] Again, these features are sensitive to crystal packing. $[Cu(tach)_2]^{2+}$ (**XV**) with ClO_4^- counteranions yields a typical elongated geometry ($Cu-N_{ax}$ = 2.353 Å, $Cu-N_{eq}$ = 2.071 Å[42]) while the nitrate salt has virtually equal Cu−N contacts ($Cu-N_{ax}$ = 2.173 Å, $Cu-N_{eq}$ = 2.164 Å[42]). However, the latter structure is, of course, an artefact of the X-ray diffraction experiment since the d−d spectra of both salts are essentially identical. The "intrinsic" structure of CuN_6 species is a tetragonally elongated octahedron and therefore the solid state structures with the largest tetragonal distortion are used for any comparisons with CLFSE/MM results (see Table 1).

Four-coordinate d^9 species are at the limit of a tetragonal elongation and are therefore less plastic. This makes them the simplest Cu^{II} systems to model as shown by the number of previous MM applications. However, crystal packing can still exert an influence. For example, the conformations of the cyclohexane ring in $[Cu(chn)_2]^{2+}$ (**XXV**) induce a 5° variation of the ligand bite angle from about 93° for the nitrate salt[58] to 87.6° for the bromide compound.[52] (Figure 7.) Overall, therefore, care is required when making comparisons between computed and "observed" structures.

Nevertheless, the CLFSE/MM approach provides satisfactory structures. The same CLFSE term as for Ni^{II} was used but with a d^9 configuration. A few of the other parameters required minor modification as described above (see Table 4). Table 3 lists a detailed comparison of Cu−N bond lengths and N−Cu−N bond angles for all 15 complexes. A full table of rms errors is available in the supplementary information.

As expected, the four-coordinate complexes, where axial interactions are minimal, are well reproduced. As for the low-spin d^8 systems, the CLFSE automatically favors a planar over a tetrahedral structure. The worst case is found for the six-membered chelate rings in $[Cu(tn)_2]^{2+}$ (**XX**) where the Cu−N bond lengths are systematically underestimated by 0.03 to 0.05 Å. In contrast, the agreement for $[Cu(deen)_2]^{2+}$ (**XXIV**) is excellent where the Cu−N distances for the substituted (observed 2.08 Å, calculated 2.10 Å) and unsubstituted (observed 2.01 Å, calculated 2.02 Å) nitrogens are rather different.

The five-coordinate complexes show a mixed performance

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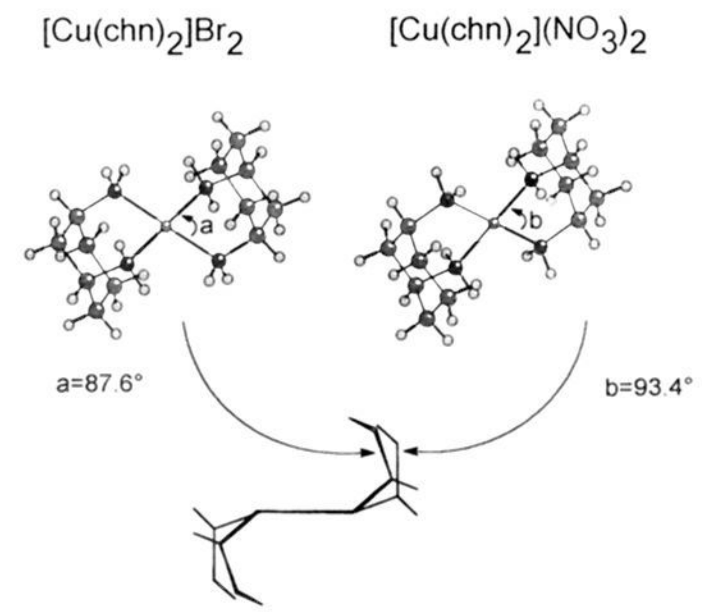

Figure 7. Molecular structures from X-ray structural analyses of two forms of $[Cu(chn)_2]^{2+}$ showing the variation of the N−Cu−N bite angle as a function of the ligand conformation. The CLFSE/MM method agrees with the structure of the bromide salt (left) rather than the nitrate salt (right).

Table 4. Complete Listing of the Force Field Parameters and Functional Forms Used in This Work[a]

Functional Forms

bond stretch: $E_{str} = D_0[1 - \exp(-e^{\alpha(r-r_0)})]^2$
angle bend: $E_{bend} = (1/2)k_\theta(\theta - \theta_0)^2$
torsion: $E_{tor} = K(1 + S(\cos n\omega)$
van der waals: $E_{vdw} = A/r^9 - B/r^6$
CLFSE: $e_\sigma = 21629 - 8235r$ (cm^{-1})

Bond Stretch

	D_0 (kcal/mol)	r_0 (Å)	α		D_0 (kcal/mol)	r_0 (Å)	α
Ni−N	80.0	2.393	0.45	N−H	93.0	0.91	2.50
Cu−N	80.0	2.283	0.45	C−C	88.0	1.50	1.92
N−C	72.0	1.49	2.20	C−H	108.6	0.97	1.60

Torsion

	K (kcal)	n	S		K (kcal)	n	S
Ni−N−C−C	0.000	0.0	0.0	H−C−N−H	1.423	3.0	−1.0
Ni−N−C−H	0.000	0.0	0.0	H−C−C−N	1.423	3.0	1.0
Cu−N−C−C	0.000	0.0	0.0	C−C−C−N	0.474	3.0	1.0
Cu−N−C−H	0.000	0.0	0.0	C−N−C−C	0.474	3.0	1.0
H−C−C−C	0.474	3.0	1.0	C−N−C−H	0.474	3.0	1.0
H−C−C−H	1.423	3.0	1.0	N−C−C−N	0.474	3.0	1.0

Angle Bend

	k_θ (kcal)	θ (°)		k_θ (kcal)	θ (°)
N−Ni−N	0.000	0.000	C−C−C	64.786	109.492
N−Cu−N	0.000	0.000	N−C−C	64.786	110.492
H−N−H	47.497	108.977	H−N−C	64.786	109.492
N−C−H	64.786	109.492	H−C−C	51.815	109.378
C−N−C	28.786	109.492	H−C−H	47.497	108.977

Van der Waals

	A	B		A	B
Ni	0.0	0.0	N	10155.9	326.517
Cu	0.0	0.0	C	14539.0	397.436
H	654.295	41.085			

[a] All energies are calculated in kcal/mol. This requires converting the CLFSE from wavenumbers.

ranging from reasonable for $[Cu(apt)]^{2+}$ (**XVII**) to apparently quite poor for $[Cu(adt)]^{2+}$ (**XVIII**) and $[Cu(papd)]^{2+}$ (**XVI**). The CLFSE/MM scheme favors SQP structures (see above). Experimentally, however, only $[Cu(apt)]^{2+}$ (**XVII**) could be even approximately described as square pyramidal.[44] The other two complexes[45,46] are closer to trigonal bipyramidal which leads to apparently poor agreement between theory and experiment. However, we attribute these discrepancies to the subtle effects of crystal packing. If the metal coordination environment is fixed at that observed crytallographically and the ligand minimized, an estimate of the strain energy difference between the "in crystal" and the "in vacuo" structures is obtained. The "in crystal" energy is, as expected, always slightly higher but by only about 1.6 kcal/mol for $[Cu(papd)]^{2+}$ (**XVI**) and $[Cu(apt)]^{2+}$ (**XVII**) and by 3.25 kcal/mol for $[Cu(adt)]^{2+}$ (**XVIII**).

The six-coordinate species are relatively well treated and are all tetragonally elongated. Given the large experimental errors associated with $[Cu(NH_3)_6]^{2+}$ (**XI**) and the apparent uncertainty regarding its actual existence,[59] the data given in Table 3 should be considered as illustrative only. The computed results for the other complexes are rather more symmetrical than the experimental data, as shown, for example, by the $Cu-N_{ax}$ distances in $[Cu(en)_3]^{2+}$ (**XII**) which are calculated to be identical (2.44 Å) while the observed values differ by 0.16 Å.[39] A similar pattern emerges for $[Cu(tcn)_2]^{2+}$ (**XIII**) and $[Cu(dien)_2]^{2+}$ (**XIV**). Again, packing forces may be to blame. Alternatively, the "observed" solid state structure may represent contributions from more than one minimum on the Mexican Hat potential energy surface.

The greater flexibility of the copper species relative to the nickel complexes is reflected in somewhat larger average rms errors of 0.024 Å and 0.897° for Cu−N distances and N−Cu−N angles, respectively. For the "organic" parts of these molecules (excluding the hydrogen atoms), the agreement for the copper species is marginally better than that for the Ni complexes. (A full listing is included in the supplementary information.) The maximum deviation of any Cu−N−C is about 3° less than the worst case for a nickel complex. The similarities across all the molecules studied here presumably reflect the common FF parameters used for the "organic" parts.

Conclusions

The Cellular Ligand Field Stabilization Energy provides a method for treating the important geometrical effects associated with the electronic energies of an incomplete d shell. In conjunction with bond-stretch and ligand−ligand nonbonding terms, the CLFSE provides a general framework for explicitly incorporating open-shell transition metals into a conventional molecular mechanics treatment for Werner-type complexes. The absence of an L−M−L angle-bend term facilitates a uniform treatment of wider ranges of coordination numbers.

The CLFSE term can be designed to mimic existing molecular mechanics force fields. However, the same CLFSE/MM force field is also able to reproduce *simultaneously* the quite different structures and Ni−N distances of octahedral high-spin and planar low-spin d^8 Ni amine complexes simply by altering the d-orbital occupations to reflect the desired spin state. The uniform treatment of both high- and low-spin systems opens the possibility for following certain types of spin crossover.

With only minor modifications, the CLFSE/MM FF provides a good treatment of four-, five-, and six-coordinate d^9 Cu amine complexes including planar CuN_4 systems and the *automatic* generation of tetragonally elongated CuN_6 centers. The Jahn−Teller effect is implicit in the CLFSE and requires no external constraints. This represents a significant first in molecular modeling of d^9 complexes. For pentacoordinate systems, the CLFSE favors a square-pyramidal geometry whereas two of the three complexes available are better described as trigonal bipyramidal. However, the apparently poorer treatment of five-coordinate complexes reflects the high flexibility or "plasticity"

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(59) See discussion in: Burton, V. J.; Deeth, R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 573−574.

of copper complexes which can result in large geometrical changes for relatively subtle variations in crystal packing.

The CLFSE/MM scheme appears to be the first general, empirical method for modeling a variety of Cu^{II} geometries and represents a significant advance in molecular mechanics methodology for d^9 copper in particular and open-shell coordination complexes in general. The next phase of this work is to extend the CLFSE term to π-bonding ligands and a wider variety of metal centers.

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Supporting Information Available: Tables of rms errors in Ni−N and Cu−N bond lengths and N−Ni−N and N−Cu−N bond angles and rms errors and maximum absolute error for Ni−N−C and Cu−N−C bond angles (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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