ogous values of the tetranuclear complex; however, this is uncertain, since the structure of the former is unknown.

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Supplementary Material Available: Complete tables of atomic coordinates, bond lengths, bond angles, hydrogen atom coordinates, anisotropic temperature factors, and temperature variation of chemical shifts (5 pages); a listing of structure factors (20 pages). Ordering information is given on any current masthead page.

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Molecular Mechanics Calculations of Transition Metal Complexes

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A molecular mechanics force field appropriate for the modeling of Cu(II), Ni(II) ($S = 1$), Co(III), Fe(III), Cr(III), Zn(II), and Rh(III) complexes with amine, carboxylate, pyridine, and thia ether ligands is presented in its entirety. The parameters comprising the force field were determined by matching a large number of strain-minimized structures with their corresponding crystal structures. Within the force field, the only parameters that were altered from one system to another were the strain-free bond length and the force constant of the metal-ligand bond. The calculations indicate that some corrections for electronic effects have to be applied in order to obtain a consistent force field.

Introduction

Molecular mechanics calculations are a routine tool in organic chemistry[1,2] and are now well established in the area of coordination chemistry,[3,4] where they have most commonly been used for the computation of structures (analysis of disordered structures[5] and prediction of unknown structures[6]), isomer and conformer ratios,[7] and metal ion selectivities.[8] A majority of studies have dealt with cobalt(III) hexaamines where a well-established force field is available,[9] and until recently, we too have been concerned solely with such systems. However, our present interest in the design of chiral systems applicable to racemate separations based on enantioselective ligand exchange,[10,11] the determination of solution structures of dimeric Cu(II) complexes,[12] and the interpretation and prediction of chromophores of transition metal ions demanded the establishment of a force field for systems other than cobalt(III) hexaamine complexes.

It has been a popular belief that metal-ligand (M-L) force constants may be obtained directly from vibrational spectra. However, one has to realize that experimental force constants are molecule-specific quantities and therefore dependent on the environment of the respective molecules, whereas molecular mechanics calculations require more general parameters. Moreover, the spectroscopic force constants apply to situations involving relatively small amplitude vibrations about a particular M-L value that may deviate considerably from the strain-free bond length. On the other hand, molecular mechanics calculations are concerned with large perturbations on a strain-free geometry. This leads to the view that molecular mechanics force constants do not necessarily represent experimentally available physical constants. Indeed, there are cases where molecular mechanics calculations have been performed based on concepts which have completely neglected the usually applied set of parameters based on the connectivity of the molecule.[13]

Force fields for several transition metal complexes have been reported including Co(III),[9] Co(II),[14] Ni(II) (both $S = 1$[15] and $S = 0$[16]), Cu(II),[17] and Pt(II),[18] although the variety of ligands considered in some of these studies tended to be rather limited. In this paper, we present force field parameters for transition metal complexes of Cr(III), Fe(III) ($S = {}^1/_2$), Co(III), Ni(II) ($S = 1$), Cu(II), Zn(II), and Rh(III) with various combinations of amine, pyridine, carboxylate, and thia ether ligands. It has not been our aim to develop an "ultimate" force field that would describe all metal-ligand interactions for all types of donor atoms, but instead we have concentrated on ligands containing the more typical "hard" donor atoms N and O and have dealt with soft donors such as S to a lesser extent. Nevertheless, the force field presented here is, we believe, either a significant improvement on previously reported force fields or it represents the first attempt to model a particular class of coordination compound with molecular mechanics.

Experimental Section

The calculations were performed with the strain minimization program MOMEC87.[19] Within the molecular mechanics framework, the structure

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Table I. Metal-Independent Bond Length Parameters

bond type	force const (mdyn Å^{-1})	strain-free bond length (Å)	bond type	force const (mdyn Å^{-1})	strain-free bond length (Å)
C–C	5.00	1.500	C_{con}=N	6.50	1.335
C–$C_{carboxyl}$	5.00	1.500	C–H	5.00	0.970
C–C_{alkene}	5.00	1.500	C_{alkene}–H	5.00	0.970
C=C	7.40	1.377	$C_{carboxyl}$1=O	9.00	1.220
C=C_{con}	7.40	1.377	$C_{carboxyl}$–O	8.00	1.290
C_{con}–C_{con}	5.00	1.470	C–S	2.64	1.820
C–N	6.00	1.490	N–H	5.64	0.910
C–N_{nitro}	5.00	1.530	N_{nitro}–O	6.50	1.213
C=N	6.50	1.335	O–H	5.00	0.910

Table II. Metal-Independent Bond Angle Parameters

bond angle type	force const (mdyn rad^{-1})	strain-free bond angle (radians)	bond angle type	force const (mdyn rad^{-1})	strain-free bond angle (radians)
C–C–C	0.45	1.911	C–C_{carbox}=O	0.25	2.067
C–C–C_{alkene}	0.45	1.911	C–C_{carbox}–O	0.25	2.067
C–C–N	0.45	1.911	O=C_{carbox}–O	0.25	2.149
C–C–S	0.69	1.911	C–N_{nitro}–O	0.45	2.059
C–C–H	0.36	1.909	C–S–C	0.50	1.740
C=C–C_{alkene}	0.97	2.094	S–C–H	0.45	1.911
C=C–N_{imine}	0.97	2.094	H–O–H	0.32	1.902
C=C–C	0.45	2.094	L–M–L	0.00	
C=C–H	0.45	2.094	M–N–C	0.20	1.920
C=N–C_{alkene}	0.97	2.094	M–N–H	0.10	1.915
C=N–C_{con}	0.97	2.094	M–N=C	0.20	2.095
C_{alkene}–C–H	0.36	1.909	M–O–C_{carbox}	0.05	2.095
C–N–H	0.45	1.911	M–O–H	0.10	1.915
C–N–C	0.45	1.911	M–S–C	0.10	1.920
H–N–H	0.33	1.902	M–O–N_{nitro}	0.32	2.095

of a molecule is modified in order to minimize its total strain energy, consisting of bond length deformation (E_b), nonbonded interactions (E_{nb}), valence angle deformation (E_Θ), torsion angle deformation (E_ϕ), and out-of-plane deformation (E_δ), (see eq 1). The functions used in our studies are presented in eqs 2–9, where k_r, k_Θ, k_ϕ, and k_δ are the force constants for bond length, valence angle, torsion angle, and out-of-plane deformations; r_0, Θ_0, and ϕ_0 are the respective strain-free values; vndr represents the van der Waals radius; and a, b, and c are variables calculated by eqs 4–6. Other terms may be included to account for electrostatic interactions and hydrogen bonding, but we have not attempted to model these effects.

$$U_{total} = \sum(E_b + E_{nb} + E_\Theta + E_\phi + E_\delta) \tag{1}$$

$$E_b = \tfrac{1}{2}k_r(r_{ij} - r_0)^2 \tag{2}$$

$$E_{nb} = ae^{-br_{ij}} - c/r_{ij}^6 \tag{3}$$

$$a = 2014(\epsilon_i\epsilon_j)^{1/2} \tag{4}$$

$$b = 12.50/(\mathrm{vndr}_i + \mathrm{vndr}_j) \tag{5}$$

$$c = (2.55(\epsilon_i\epsilon_j)^{1/2}(\mathrm{vndr}_i + \mathrm{vndr}_j)^6)/144 \tag{6}$$

$$E_\Theta = \tfrac{1}{2}k_\Theta(\Theta_{ijk} - \Theta_0)^2 \tag{7}$$

$$E_\phi = \tfrac{1}{2}k_\phi(1 + \cos(m(\phi_{ijk} + \phi_{off}))) \tag{8}$$

$$E_\delta = \tfrac{1}{2}k_\delta\delta^2 \tag{9}$$

No symmetry restrictions were imposed on the local coordination sphere, and nonbonded interactions involving the metal center were neglected. This approach has also been taken by others in earlier force field calculations of transition metal complexes.[3,9] Input coordinates were obtained from crystal structure data or produced with the graphics package SMILE.[20] The strain-free bond length and force constant for each type of M–L bond were adjusted until an optimal agreement between calculated and experimental structure was obtained throughout the entire range of available structures.

Results and Discussion

The components of the force field describing intraligand interactions were not altered throughout the series of systems studied. The majority of parameters dealing with the organic framework have been employed in earlier purely organic[2] force field calculations and also in transition metal complex force fields[9] or have been developed for this work where adequate data were not available in the literature. The complete list of intraligand force

Table III. Torsion Angle and Out-of-Plane Deformation Parameters

bond torsion	k_ϕ (mdyn rad^{-1})	m	ϕ_{off} (rad)
C–C	0.0017	3	0.0
C–$C_{carboxyl}$	0.0010	6	0.5237
C–C_{alkene}	0.0005	6	0.5237
C=C	0.0030	2	1.5708
C–N	0.0010	3	0.0
C–N_{imine}	0.0020	6	0.5237
C–N_{nitro}	0.0025	6	0.5237
C=N	0.0030	2	1.5708
C–S	0.0008	3	0.0
$C_{carboxyl}$–O	0.0045	2	1.5708
C_{con}–C_{con}	0.0300	2	1.5708

plane of atoms	k_δ (mdyn Å^{-1})
C–$C_{carboxyl}$–O–O	0.12
C–N_{nitro}–O–O	0.12
N=C–H–H	0.12

Table IV. Nonbonded Interaction Parameters

atom	vndr (Å)	ϵ	atom	vndr (Å)	ϵ
C	1.90	0.044	O	1.70	0.055
H	1.44	0.024	S	2.00	0.185
N	1.80	0.050			

Chart I

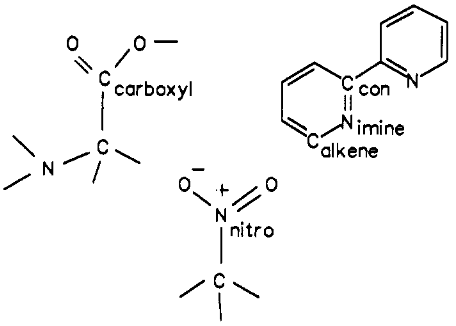

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Table V. Metal-Dependent Bond Length Parameters

bond type	force constant (mdyn Å^{-1})	strain-free bond length[a] (Å)
Co(III)–N$_{amine}$	1.75	1.905 (1.905)
Co(III)–N$_{amine(carboxyl)}$	1.75	1.915
Co(III)–N$_{imine}$	1.75	1.865
Co(III)–O$_{carboxylate}$	1.40	1.860
Ni(II)–N$_{amine}$	0.60	2.090 (2.050)
Ni(II)–N$_{amine(carboxyl)}$	0.60	2.035
Ni(II)–N$_{imine}$	0.60	2.025
Ni(II)–O$_{carboxylate}$	0.65	2.040
Cr(III)–N$_{amine}$	1.10	2.045
Cr(III)–N$_{imine}$	1.00	1.985
Fe(III)–N$_{amine}$	1.70	1.950
Fe(III)–N$_{imine}$	1.70	1.925
Zn(II)–N$_{amine}$	0.35	2.220
Rh(III)–N$_{amine}$	1.75	2.050
Cu(II)–N$_{amine}$	0.60	1.970 (1.940)
Cu(II)–N$_{imine}$	0.60	1.940
Cu(II)–O$_{carboxylate}$	0.80	1.900
Cu(II)–S	0.60	2.290
Cu(II)–O$_{nitro}$	0.10	2.500
Cu(II)–O$_{axial\ 6\text{-}coord}$	0.10	2.500
Cu(II)–O$_{axial\ 5\text{-}coord}$	0.10	2.150

[a] Values in parentheses represent M–N strain-free bond length in the presence of pyridyl ligands.

field parameters is given in Tables I–IV. The nomenclature employed for the carbon, nitrogen, and oxygen atoms is defined in Chart I.

The metal-dependent force field parameters are presented in Table V. No constraints were placed on the L–M–L angles (i.e., $k_\theta = 0$); instead, the 1,3 nonbonded repulsions of the donor atoms accounted for the geometry of the coordination sphere. We have found that the same M–X–H and M–X–C (X = N, O, S) angle force contants may be employed regardless of the metal ion. This approach has the advantage that the only parameters that require changing from one system to another are the strain-free M–L bond lengths (r_0) and force constants (k_r) appropriate for the metal ion in question. It may be seen that the different electronic properties of systems with various d-electron configurations are manifested in these parameters. However, values of r_0 and k_r particular to one type of coordinate bond cannot be assumed to be transferable to another system containing the same M–L bonds when significant electronic or electrostatic effects are introduced via other ligands. We have determined various corrections to some r_0(M–L) values due to the influence of these effects.

Unless otherwise specified, all strain energy minimized structures reproduced the observed X-ray structures to a tolerance of 0.02 Å in the M–L bond lengths and 3° in the L–M–L angles. It was apparent that several crystal structures used in the development of the present force field revealed the symmetry of the complex in the crystal lattice to be lower than one would anticipate. Effects such as these are attributable to hydrogen bonding and packing within the lattice and were not modeled. In such instances, there tended to be a larger than normal discrepancy between observed and calculated structures, but the "average" structure determined by the strain minimization routine was always an adequate representation of the observed structure. Space restrictions do not allow a complete listing of calculated bond lengths and angles for all structures; therefore we have merely listed the observed and calculated M–L bond lengths (Tables VI–XI). These tables contain the complete list of structures used in the parametrization. Comparison between experimental and calculated structures revealed the purely organic components of the ligand to be well matched, as one would intuitively expect if the observed and calculated positions of the metal and the donor atoms are in agreement.

A. "Octahedral" Complexes. (i) Hexaamine Complexes. Hexaamine complexes of cobalt(III), cobalt(II), and high-spin nickel(II) have been the only hexaamine systems to be modeled with molecular mechanics in the past. Herein we report a force field appropriate for modeling chromium(III), iron(III), nickel(II), rhodium(III), and zinc(II) hexaamine complexes. The relevant r_0 and k_r parameters are presented in Table V. The types of complexes that have been modeled range from hexaammine, through tris(diamines) and bis(triamines), (both cyclic and linear) to sexidentate macrocyclic hexaamines. The variety of ligands resulted in a wide range of M–N bond lengths in order to thoroughly test the r_0 and k_r parameters for the coordinate bond. Distortions from octahedral symmetry, such as trigonally twisted and tetragonally distorted geometries, were also reproduced by the force field calculations.

(ii) Hexaimines and Mixed Amine/Imine Complexes. All structures modeled with this force field contained polypyridyl-based ligands (2,2′-bipyridyl, 2,2′,2″-terpyridyl, phenanthroline), since these ligands represent the most commonly studied bi- and tridentate imine ligands. The M–N parameters appropriate to calculation of chromium(III), low-spin iron(III), cobalt(III), and high-spin nickel(II) imine complexes were developed, and the r_0 and k_r values are given in Table V. In the cases where adequate structural data were available, a correction to the r_0(M–N,amine) value as a result of the presence of the pyridyl ligands was determined. The justification behind this is merely qualitative; that is, π-back-bonding to pyridyl ligands increases the "acidity" of the metal center and thus other donors may approach the metal more closely.

(iii) Cobalt(III) and Nickel(II) Carboxyl Amines. The force field for hexaamine cobalt(III) complexes[9] is fairly well established. However, the same parameters describing Co–N interactions in hexaamine complexes are not necessarily transferable to systems where ligands other than amines are present, in particular carboxylato ligands. We have therefore extended the hexaamine r_0(Co–N) value for the calculation of carboxylato amine complexes of cobalt(III), but the Co–N force constant was not altered (Table V). The origin of this shift in the r_0 value is presumably due to negative charge delocalization from the carboxylates onto the metal center, π-donation by the ligands, or a mixture of both these effects. We have not incorporated any parameters modeling electrostatic effects, since the shift in Co–N bond lengths may be simply, and effectively, modeled by adjusting the r_0 value. Separation of this effect into electronic and electrostatic contributions would be, in principle, an acceptable approach provided that reliable parameters could be obtained. Deduction of these parameters is, however, a complicated matter. There is a strong case for keeping the parametrization as simple as possible, and in the present case, we have chosen to model any electrostatic

Table VI. Average Strain Energy Minimized (and Observed) M–N Bond Lengths (Å) for Hexaamine Complexes

	diammac[a]	diamsar	(en)$_3$	(tacn)$_2$	(tn)$_3$	(tach)$_2$	(dien)$_2$[b]	(NH$_3$)$_6$	dtne
Cr(III)	2.05, 2.06 (2.04, 2.07)[27]	2.07 (2.07)[28]	2.08 (2.07)[29]		2.10 (2.09)[30]		2.06, 2.08, 2.09 (2.06, 2.08, 2.09)[31]	2.08 (2.08)[32]	
Fe(III)	1.97, 1.98 (1.97, 1.98)[33]	2.00 (2.00)[34]		2.00 (2.00)[35]					2.01 (2.00)[36]
Ni(II)	2.07, 2.11 (2.07, 2.12)[37]	2.11 (2.11)[34]	2.13 (2.13)[38]	2.12 (2.10)[39]	2.16 (2.14)[40]	2.13 (2.13)[41]	2.10, 2.14, 2.15 (2.07, 2.13, 2.18)[42]		
Zn(II)	2.11, 2.20 (2.10, 2.21)[43]	2.20 (2.19)[34]	2.23 (2.22)[44]						
Rh(III)	2.05, 2.06 (2.05, 2.06)[45]		2.07 (2.06)[46]					2.07 (2.07)[47]	

[a] M–N(sec), M–N(prim). [b] M–N(sec), M–N(prim), M–N(prim).

Table VII. Strain Energy Minimized (and Observed) M–N Bond Lengths (Å) for Hexaimine or Mixed Amine/Imine Complexes

	$(bipy)_3$	$(phen)_3$	$(terpy)_2$[a]	$(dipa)_2$[b]
Fe(III)	1.97 (1.96)[48]	1.97 (1.97)[49]		
Cr(III)	2.03 (2.04)[50]		2.01, 2.04 (1.98, 2.05)[51]	
Ni(II)	2.08 (2.11)[52]		2.06, 2.09 (2.01, 2.12)[53]	2.08, 2.11 (2.10, 2.12)[54]
Co(III)	1.91 (1.93)[55]		1.90, 1.93 (1.86, 1.93)[56]	1.91, 1.96 (1.93, 1.96)[54]

[a] Bond lengths correspond to central and terminal N-donors, respectively. [b] Bond lengths refer to pyridyl and amine bonds, respectively.

Table VIII. Average Strain Energy Minimized (and Observed) M–N and M–O Bond Lengths (Å) for Cobalt(III) and Nickel(II) Carboxyl Amine Complexes

	(ppm)(ala)	acammac	α-(edda)-(en)	β-(edda)-(en)	$(gly)_2$(β-ala)
Co–N	1.97 (1.98)[57]	1.95 (1.95)[58]	1.95 (1.94)[59]	1.95 (1.96)[59]	1.96 (1.94)[60]
Co–O	1.90 (1.90)	1.90 (1.90)	1.90 (1.89)	1.90 (1.91)	1.89 (1.90)

	tacnta	dota	edta
Ni–N	2.06 (2.04)[61]	2.13 (2.15)[62]	2.07 (2.06)[63]
Ni–O	2.06 (2.07)	2.07 (2.03)	2.05 (2.07)

effects simply by adjusting the r_0(M–N) bond lengths; i.e., any electrostatic effects are absorbed into the parameters modeling electronic effects. The force field satisfactorily reproduces the structures of carboxylato pentaamine, dicarboxylato tetraamine, and tricarboxylato triamine complexes of cobalt(III), each with the same value of r_0(Co–N). This is an important factor since one might anticipate that the introduction of successive carboxylates might have an additive effect on the value of r_0(Co–N), particularly if electrostatic effects are significant, but such was not the case. The Co–O parameters for r_0 and k_r gave a satisfactory fit to the experimental structures.

Similarly the Ni–N strain-free bond length required adjustment from its hexaamine value in order to model complexes that possessed carboxylato ligands (Table V). Surprisingly, a much smaller r_0(Ni–N) value than that employed for the hexaamine calculations was found to be appropriate (cf. the Co(III) system). It was again found that a single r_0(Ni–N) value sufficed in modeling complexes with two, three, and four coordinated carboxylates. The Ni–O parameters were similar to those describing the Ni–N bonds.

B. Complexes of Copper(II). The pseudooctahedral complexes discussed thus far may all be satisfactorily modeled with molecular mechanics without consideration of any second-order electronic effects that might lower the symmetry of the complex. It has been assumed in the previous sections that all sites within the coordination sphere are equivalent. Therefore, in the absence of significant intramolecular strain, complexes containing six identical donor atom types will always exhibit octahedral symmetry. In complexes of metal ions where strong Jahn–Teller coupling is commonly found, especially copper(II), one cannot assume, to a first approximation, that the complex will have octahedral symmetry; specifially, all M–L bonds cannot be identical. Complexes of copper(II) often exhibit a tetragonally distorted octahedral geometry (usually in the form of axial elongation), but also trigonal prismatic, square-based pyramidal, trigonal bipyramidal, tetrahedral, and even genuinely square planar complexes of copper(II) have been characterized structurally. There do exist complexes that exhibit apparent octahedral symmetry, but such examples have been assigned as averages of tetragonal structures as a result of a dynamic Jahn–Teller effect.[21]

It is a fundamental assumption of molecular mechanics that one knows the coordination number of the complex before calculating the strain energy minimized structure. As illustrated above, copper(II) may accommodate any number of donor atoms from four to six, so unless one can predict the coordination number of the complex beforehand, the strain energy minimized structure cannot be expected to reproduce the observed structure. Within certain limits, one can make some assumptions regarding the coordination number of these complexes. The preferred geometries of copper(II) complexes of quadridentate macromonocyclic ligands are fairly predictable. If the macrocyclic ring comprises more than 13 atoms, then the geometry of the complex is generally tetragonally distorted octahedral (hereafter referred to as tetragonal). Conversely, 12- and 13-membered macrocycles generally prefer square pyramidal geometries, since the smaller hole sizes of these macrocycles do not comfortably encircle the metal ion, although there are exceptions to both of these "rules". Geometries and coordination numbers of acyclic copper(II) complexes are much more difficult to predict. In some cases, $[Cu(NH_3)_4]^{2+}$ being a pertinent example, the same tetraamine complex of copper(II) may exhibit either a tetragonal or a square pyramidal geometry in the solid state.[22] In addition, the average Cu–N bond lengths in tetragonal $[Cu(NH_3)_4]^{4+}$ complexes have been found to vary from ca. 2.00 to 2.05 Å, depending on the counter ions present.[23] The present force field was developed by fitting known structures (of known coordination number) with the appropriate trial coordination sphere (i.e. four-, five-, or six-coordinate). Use of the force field in predicting unknown structures of copper(II) complexes will necessarily involve a prediction of the coordination number prior to calculation.

(i) Axial Cu–O Interactions. For complexes of tetragonal or square pyramidal geometry, axial interactions are generally with aqua ligands, halides, or oxo anions such as perchlorate, sulfate, or nitrate. What is perhaps surprising is that the r_0(Cu–L) and k_r(Cu–L) values for axial ligands do not appear to be dependent on the type of axial donor atom, which is usually the most important factor in the consideration of an M–L bond. Electronic effects from the axial donors are evidently small, and the examples modeled in this study reveal similar axial Cu–L bond lengths with N^-, O^-, F^-, and Cl^- donors. However, when considering donor atoms of disparate sizes, e.g., Cl and I, one cannot assume that they both will refine to M–L bond lengths of similar magnitude. Ligating atoms with large van der Waals radii, such as I^-, are not commonly encountered in complexes of copper(II), so such effects may be considered to be exceptional. In order to simplify the force field, only two types of axial Cu–L bonds have been included, one for tetragonal complexes and the other for five-coordinate complexes regardless of the type of donor atoms in the equatorial sites. For the purpose of generality, all axial ligands were refined as water molecules. This is quite realistic since aqua ligands invariably are the occupants of axial sites of copper(II) complexes in aqueous solution.

The r_0(Cu–O) and k_r(Cu–O) parameters for five-coordinate tetraamine copper(II) complexes were 2.150 Å and 0.1 mdyn $Å^{-1}$, respectively. A longer r_0(Cu–O) value (2.500 Å) was employed in calculations of tetragonal complexes, implying a significant electronic effect being in operation when the geometry of the coordination sphere changes from square pyramidal to tetragonal. The discrepancies between observed and calculated Cu–O bond lengths are greater than one would normally tolerate for M–L bond lengths; however, the agreement is remarkably good when one considers the relative simplicity of the present approach.

A popular approach to the modeling of axial Cu–O bonds has been to "fix" dummy atoms in axial sites, generally by setting the Cu–O force constant to an unrealistically large value and adjusting the r_0 value to the crystallographically determined Cu–O bond length. This is a rather dubious procedure, since it not only requires a prior knowledge of the geometry and coordination number of the complex, but the Cu–O axial bond length must

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Table IX. Strain Energy Minimized (and Observed) Cu-N and Cu-O Bond Lengths (Å) for tetraamine Copper(II) Complexes

	$Cu-N_{amine}$	$Cu-O_{axial}$		$Cu-N_{amine}$	$Cu-O_{axial}$
$(en)_2$	2.00 (2.02)[64]	2.54 (2.56)	$[12]aneN_4$	2.03 (2.02)[68]	2.16[b] (2.18)
$(NH_3)_4$	2.01 (2.01)[22]	2.54 (2.53)	$mn[13]aneN_4$	1.97 (1.95)[69]	2.64 (2.65)
ppm	2.01 (2.02)[65]	2.49 (2.80)	$mn[14]aneN_4$	2.02 (2.01)[70]	2.58 (2.56)
rac-$(ahaz)_2$	2.02[a] (2.01)[25]		$mn[15]aneN_4$	2.04 (2.04)[71]	2.45,[c] 2.52 (2.44,[c] 2.58)
(*S*,*S*)-$(ahaz)_2$	2.01 (2.01)[66]	2.32[b] (2.44)	$mn[16]aneN_4$	2.01 (2.02)[71]	2.70, 2.66 (2.70, 2.58)
$mn[15.2]aneN_4$	2.06 (2.05)[66]	2.15[b] (2.22)			

[a] Four-coordinate. [b] Five-coordinate. [c] Coordinated nitro group.

Table X. Average Strain Energy Minimized (and Observed) Bond Lengths (Å) for Copper(II) Complexes with Amine, Imine, and Carboxylate Ligands

	$Cu-N_{amine}$	$Cu-N_{imine}$	$Cu-O_{carboxylate}$	$Cu-O_{axial}$
ndap	1.98 (1.98)[72]	1.95 (1.97)		2.59 (2.70)
$(eap)_2$	2.00 (2.01)[73]	1.99 (2.03)		2.67 (3.6)[a]
$(bipy)_2$		1.99 (1.99)[75]		2.60 (2.62)
mnpgly	1.98 (1.98)[76]		1.92 (1.92)	2.30 (2.60)
rac-mnpala	1.98 (1.99)[76]		1.92 (1.93)	2.56 (2.60)
(*S*,*S*)-mnpala	1.98 (1.98)[76]		1.92 (1.92)	2.32 (2.70)
mnpbala	1.98 (2.01)[77]		1.92 (1.97)	2.31 (2.28)

[a] Iodo ligand modeled as a water molecule.

Table XI. Average Strain Energy Minimized (and Observed) Bond Lengths (Å) for Thia Ether Copper(II) Complexes

	Cu-S	$Cu-O_{axial}$	Cu-N
$[12]aneS_4$	2.34 (2.33)[78]	2.15 (2.11)	
$[13]aneS_4$	2.33 (2.33)[78]	2.14 (2.14)	
$[14]aneS_4$	2.29 (2.30)[79]	2.58 (2.65)	
$[16]aneS_4$	2.34 (2.36)[78]	2.54 (2.48)	
$mn[14]aneN_2S_2$	2.31 (2.30)[80]	2.59 (2.58)	2.01 (2.01)

also be known—thus obviating the need for molecular mechanics calculations altogether. Furthermore, it is not acceptable to fix the Cu-O bond lengths to some arbitrary value. Examination of the available structures shows that the axial Cu-O bond lengths are quite significantly affected by the neighboring equatorial ligands. Variations from ca. 2.15 to 2.60 Å are known for square pyramidal tetraamine complexes, whereas Cu-O bonds in the range of 2.50-2.80 Å have been observed in tetragonal copper(II) complexes. It is important to note that one must generally include these axial ligands (whether they are fixed or not) if the tetragonal geometry of the complex is to be maintained. If no axial ligands are considered in the strain minimization procedure, then the (four-coordinate) complex will generally undergo a distortion toward tetrahedral geometry as a result of van der Waals repulsions of the equatorial donor atoms. Tetrahedral distortions may still be observed in the presence of axial ligands when steric effects of the in-plane ligands are significant.

(ii) Tetraamine Complexes. Numerous tetraamine complexes of copper(II), containing both acyclic and macrocyclic ligands, have been characterized structurally, and we have determined general r_0 and k_r values for the Cu-N (amine) bond (Table V). However, applying the strain minimization routine to some structures revealed some unusual geometrical changes. The crystal structure of $[Cu(NH_3)_4](SO_4)\cdot H_2O$ defines the cation as having a square pyramidal geometry (Cu-N 2.031 Å, Cu-O 2.34 Å).[22] However, the strain energy minimized structure of $[Cu(NH_3)_4(OH_2)]^{2+}$ was found to be trigonal bipyramidal and not square pyramidal. Such a result indicates that, in the absence of any constraints on the N-Cu-N and O-Cu-N bon angles (via chelate rings or the bonding angle force constant), the strain energy minimized structures of five-coordinate copper(II) complexes will refine to a trigonal bipyramidal geometry, purely as a result of nonbonded repulsions between the N and O donors. In any case, the present example is not particularly relevant, in that the aqueous solution structure of $[Cu(NH_3)_4]^{2+}$ is neither square pyramidal or trigonal bipyramidal but has been found to be tetragonally distorted octahedral based on electron paramagnetic resonance studies.[24] Moreover, modeling the six-coordinate complex $[Cu(NH_3)_4(OH_2)_2]^{2+}$ reproduces the crystal structure of $[Cu(NH_3)_4](SeO_4)$.[22]

Constrained tetraamines such as tetraaza macrocycles prefer square pyramidal to trigonal bipyramidal geometries, since the former allows the four macrocyclic amines to remain coplanar. The strain energy minimized structures of five-coordinate complexes of small macrocyclic tetraamines do, in this case, refine to square pyramidal geometries. The above discussion does not neglect the existence of genuinely square planar copper(II) complexes; in fact there are several known examples. The strain energy minimized structure of the genuinely square planar tetraamine complex *rac*-bis(3-azacycloheptaneamine)copper(II) does reproduce the crystal structure[25] in the absence of axial ligands. In this special case, interligand steric effects outweigh N···N repulsions in the complex, and the four N-donors remain coplanar.

(iii) Tetraimines, Diimine Diamines, and Dicarboxyl Diamines. Modeling of structures of copper(II) amine complexes where π-acceptor ligands such as imines are present necessitated the employment of a contracted Cu-N (amine) strain-free value (Table V) in order to reproduce experimentally determined structures. The relevant Cu-N (imine) and Cu-O (carboxylate) parameters are also given in Table V. It was found that the Cu-N and axial Cu-O parameters used in the tetraamine complex force field were able to be employed in the present calculations without corrections due to the carboxyl groups (cf. Co(III) and Ni(II) parameters).

(iv) Thia Ethers and Thia Ether Amines. We have modeled the structures of several macrocyclic thia ether and thia ether amine complexes of copper(II). An earlier report concerning molecular mechanics calculations of thia ether complexes of copper(II) adopted a quite different set of force field parameters,[26]

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and moreover, the positions of the axial ligands were not refined. We have adopted a shorter strain-free Cu–S value and a different force constant (Table V). There was found to be no significant π-bonding effect on the r_0(Cu–N) value due to the presence the S-donors.

Conclusions

The force field presented herein allows prediction via molecular mechanics of the structures of a variety of hexaamine, mixed amine/imine, and amine/carboxylate complexes of the more commonly encountered "octahedral" transition metal ions. A new approach to the calculation of copper(II) complexes has been presented. Specifically, the refinement of the positions of the "axial" donor atoms allows one to predict the structures of copper(II) complexes without any constraints being placed on the coordination sphere. Although the accuracy of the positions of the axial donor atoms is not of the same order as that obtained with other calculated M–L bonds, the errors inherent to this method do not appear to propagate to the remainder of the copper(II) complex.

It has been shown that employment of the present force field within the strain minimization routine may quite accurately predict the crystal structures of a wide range of coordination compounds, the majority within experimental error. The structures fitted in this work represent the widest range of available geometries. Systems exhibiting either a little or a great degree of intraligand strain were reproduced equally well. Therefore, one may determine, with some accuracy, the structure of any of a wide variety of coordination compounds prior to their crystal structure being determined or even before they have been synthesized. This is an obvious advantage in the structural design of transition metal complexes. The accuracy of thermodynamic predictions of complex formation by molecular mechanics is more difficult to assess, but the present force field has already been successfully employed in the quantitative prediction of isomer distributions of Co(III) and Ni(II) complexes, where experimental work confirmed molecular mechanics predictions.[10,11]

Molecular mechanics is now a well-established technique in the field of coordination chemistry. Its applications, to date, have been many and varied, and it is anticipated that these will expand further in the future. A hindrance to the expansion of this field has been the emphasis, to the virtual exclusion of all other systems, on cobalt(III) and nickel(II) amine complexes. It was this apparent neglect that prompted the present work, and it is hoped that this will prompt others into molecular mechanics calculations of an increasingly wide range of coordination compounds.

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Glossary

acammac	6-amino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6-carboxylate
ahaz	2-azacycloheptanamine
ala	alanate (2-aminopropanoate)
β-ala	β-alanate (3-aminopropanoate)

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bipy	2,2′-bipyridyl
diammac	6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine
diamsar	3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane-1,8-diamine
dien	bis(2-aminoethyl)amine
dipa	bis(2′-pyridyl)methanamine
dota	1,4,7,10-tetraazacyclododecane-*N,N′,N″,N‴*-tetraethanoate
dtne	1,2-bis(1,4,7-triaza-1-cyclononyl)ethane
eap	2′-pyridylethanamine
edda	ethane-1,2-diamine-*N,N′*-diethanoate
edta	ethane-1,2-diamine-*N,N,N′,N′*-tetraethanoate
en	ethane-1,2-diamine
gly	glycinate (aminoethanoate)
mn[13]aneN$_4$	12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane
mn[14]aneN$_4$	6-methyl-6-nitro-1,4,8-11-tetraazacyclotetradecane
mn[15]aneN$_4$	10-methyl-10-nitro-1,4,8,12-tetraazacyclopentadecane
mn[16]aneN$_4$	3-methyl-3-nitro-1,5,9,13-tetraazacyclohexadecane
mn[15.2]aneN$_4$	7-methyl-7-nitro-1,5,9,13-tetraazabicyclo-[11.2.2]heptadecane
mn[14]-aneN$_2$S$_2$	6-methyl-6-nitro-1,8-diaza-4,11-dithiacyclotetradecane
mnpala	5-methyl-5-nitro-2,5,8-trimethyl-5-nitro-3,7-diazanonanedioate
mnpbala	6-methyl-6-nitro-4,7-diazaundecanedioate
mnpgly	5-methyl-5-nitro-3,7-diazanonanedioate
[12]aneN$_4$	1,4,7,10-tetraazacyclododecane
[12]aneS$_4$	1,4,7,10-tetrathiacyclododecane
[13]aneS$_4$	1,4,7,11-tetrathiacyclotridecane
[14]aneS$_4$	1,4,8,11-tetrathiacyclotetradecane
[16]aneS$_4$	1,5,9,13-tetrathiacyclohexadecane
ndap	*N,N′*-bis(2′-pyridylmethyl)-2-methyl-2-nitropropane-1,3-diamine
phen	*o*-phenanthroline
ppm	*N,N′*-bis(2′-pyrrolidinylmethyl)propane-1,3-diamine
tach	*cis,cis*-cyclohexane-1,3,5-triamine
tacn	1,4,7-triazacyclononane
tacnta	1,4,7-triazacyclononane-*N,N′,N″*-triethanoate
terpy	2,2′,2″-terpyridyl
tn	propane-1,3-diamine

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Determination of Solution Structures of Binuclear Copper(II) Complexes

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A simple and efficient method for the determination of solution structures of weakly coupled binuclear copper(II) complexes is described. The technique involves the combination of molecular mechanics and EPR spectroscopy and has been applied to the binuclear copper(II) complexes of 5,5′-bis(3,7-dehydro-3,7-diazanonane-4,6-dione-1,9-diamine) (L^1), 5,5′-bis(3,7-diazanonane-1,9-diamine) (L^2), and 5-methyl-5-nitro-3,7-diazanonanedioate (L^3). The complexes $[Cu_2L^1]\cdot 10H_2O$ and $[Cu_2L^2](ClO_4)_4$ were also characterized by X-ray crystallography. $[Cu_2L^1]\cdot 10H_2O$: space group $P\bar{1}$; $a = 7.669$ (2), $b = 8.757$ (3), $c = 10.596$ (2) Å; $\alpha = 79.57$ (3), $\beta = 83.36$ (2), $\gamma = 89.17$ (3)°. $[Cu_2L^2](ClO_4)_4$: space group $P3_221$; $a = 13.671$ (2), $b = 13.671$ (2), $c = 13.929$ (2) Å. There is excellent agreement between the X-ray crystal structures and the structures predicted by molecular mechanics and EPR spectroscopy. Electrochemical properties of the binuclear complexes are also reported.

Introduction

The pursuit of structures of large polynuclear coordination compounds, particularly those containing copper(II), has been largely motivated by a rather important role that such compounds play in bioinorganic systems.[4] Over the last decade or so, advances in protein X-ray crystallography have led to the solution of previously inaccessible structures of large biologically important molecules.[5] However, there are still problems associated with this technique, e.g., difficulties in obtaining X-ray quality crystals in addition to solution and precise refinement of the structure. Moreover, it should not be forgotten that the result of a crystal structure is not necessarily comparable with what one might find in solution. Solution techniques such as EXAFS have been applied to the determination of internuclear distances of large polynuclear complexes;[6] however, information such as the orientation of two coordination sites with respect to each other is beyond the scope of this method. NMR spectroscopy may give an insight to the connectivity and conformational geometry within large molecules such as metalloproteins;[7,8] however, a correct interpretation of the experimental spectrum is quite labor intensive. At this time, comparatively few solution structures of high molecular weight, biologically relevant molecules have been determined by NMR techniques alone.

Molecular mechanics calculations have been successfully applied to the determination of structures of small organic and coordination compounds.[9-12] The accuracy of such calculations generally leads to structures that are in agreement with those obtained from X-ray crystallographic studies, within experimental error. In most molecular mechanics studies of mononuclear complexes, a complete conformational analysis is necessary. However, when one considers high molecular weight systems, which generally possess greater conformational freedom, a somewhat restricted analysis must be adopted in order that the problem remains tractable. The relative strain energies of the isomers may give an indication of their abundance, but this alone is insufficient for a definite assignment of the solution structure. The same ambiguities are inherent to molecular mechanics calculations as to X-ray crystallography; i.e., there is still no guarantee that the solid-state and solution structures are the same. Therefore, additional spectroscopic evidence is necessary in order to corroborate predictions made by molecular mechanics calculations.

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