153. The Directionality of d-Orbitals and Molecular-Mechanics Calculations of Octahedral Transition-Metal Compounds

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A novel approach to modeling the angular geometry about the metal centre in transition-metal complexes, using a variation of classical molecular-mechanics calculations, is presented. The approach is based on the combination of 1,3-nonbonded interactions around the metal centre and a harmonic sine function with a ligand-field-dependent force constant for the L–M–L′ terms. Force-field parameters for four-, five-, and six-coordinated first-row transition-metal coordination centres and a variety of ligands containing N-, S-, and O-donor sets are given. The new 'electronically doped' force field is shown to generally lead to computed structures with higher accuracy than those obtained when the coordination geometries are modeled with 1,3-nonbonded interactions alone.

Introduction. – The relatively slow development of molecular-mechanics modeling of metal complexes is mainly due to the great variety of oxidation states, coordination numbers, and coordination geometries that are accessible for transition-metal centres, and this is a result of the partly filled d-orbitals [1]. Even with a given oxidation state and coordination number, and with systems where more pronounced effects such as *Jahn-Teller* distortions or *trans*-influences are absent, modeling of coordination geometries is not trivial. The problem that the angular distribution of the ligand atoms around a metal centre requires a function with various minima (*e.g.* 90/180° for square-planar and octahedral geometries, and 90/180/120° for trigonal bipyramidal coordination) has been solved with four fundamentally different approaches: *i*) representation of ligand–metal–ligand valence-angle bending by purely electrostatic or *van der Waals* terms [2] [3]; *ii*) search procedures based on the starting geometry followed by the assignment of a particular function and/or force field to the coordination angle [4]; *iii*) modeling of coordination angles with trigonometric potential-energy functions having multiple minima, similar to those used for torsional angle potentials [5]; and *iv*) computation of the angular geometry with models involving valence bond [6] or ligand-field [7] approaches.

We have developed force fields for a large series of transition-metal compounds including primarily first transition-metal-row centres and N-, S-, and O-donor groups, using 1,3-nonbonded interactions to model the coordination geometries [3b]. This parameterization has been tested successfully with many problems involving the modeling of structural, thermodynamic, and spectroscopic features [1b] [8]. However, we have recently found that the agreement between experimental and computed angular geometries of metal complexes may be unacceptably poor for applications involving

spectroscopic properties [9]. This particular problem occurred with our recently developed MM-AOM technique, where calculated structures are used as a basis for AOM (angular overlap model) calculations to estimate spectroscopic properties [8–11]. Here, an accurate angular geometry is of critical importance, and relatively large inconsistencies occurred, especially with octahedral Cr^{III} and Ni^{II} systems having appreciably large ligand fields and comparably long metal–ligand distances. We now present a modified force field for hexacoordinate transition metal complexes. The simple addition of a harmonic sine function with a ligand-field-dependent generic force constant to model the L–M–L' terms leads to an 'electronically doped' molecular-mechanics force field. The advantages over more elaborate methods [6] [7] are that our approach requires only minimal changes to existing commercial programs and extensive force fields.

The Ligand-Field Approach for the d-Orbital Directionality. – Due to the generally successful behavior of the model involving 1,3-nonbonded interactions, and since *van der Waals* interactions between coordinated atoms must be of some importance, we have retained the functions and their parameterization as before and added a new potential as an electronic perturbation. For octahedral geometries, the ligands are located along the cartesian x, y, and z axes. The simplest function with minima at 90 and 180° is a harmonic sine function of 2θ, where θ is the ligand–metal–ligand angle (*Eqn. 1*). With the factor of

$$E_\theta = 1/8 \, k_\theta \sin^2(2\theta) \tag{1}$$

1/8, the shape of the potential is in the vicinity of the energy minimum, identical to that of the widely used harmonic potential of *Eqn. 2*.

$$E_\theta = 1/2 \, k_\theta \, (\theta - \theta_0)^2 \tag{2}$$

The steepness of the harmonic sine function, determined by k_θ, i.e., the degree of the electronic perturbation to the total strain energy, must depend on the ligand field of the chromophore which may be quantified on the basis of simple ligand-field theory. The effect of the d-orbital occupancy of the metal centre is given by the linear dependence of the ligand-field stabilization energy nDq between the extreme values for d^0, high-spin d^5 and d^{10} electronic ground states ($n = 0$), d^3 and d^8 ($n = 12$), and low spin d^6 ($n = 24$), when spin-pairing energies are neglected. The ligand-field strength (spectrochemical series) may then be related to the metal–ligand bond-stretching force constant of the two relevant ligand atoms, k_{ML} and $k_{ML'}$. Thus, k_θ is a generic force constant, computed by *Eqn. 3*, where c is a normalization parameter, fitted in our case to a series of Co^{III}-hexaamine complexes, n accounts for the d-orbital occupancy and $1/2(k_{ML} + k_{ML'})$ represents the spectrochemical series of the metal ion and the ligand atoms.

$$k_\theta = cn^{1/2}(k_{ML} + k_{ML'}) \tag{3}$$

Results and Conclusion. – *Eqn. 1* was coded into our molecular-modeling package MOMEC [12], and the force constants k_θ were fitted to a series of Co^{III}-hexaamines and checked with a large series of Ti^{IV}, Cr^{III}, low-spin Fe^{III}, Co^{III}, Co^{II}, Ni^{II}, Cu^{II} (hexa-, penta-, and tetracoordinate), and Zn^{II} (octahedral and tetrahedral) complexes with various donor groups (52 structures altogether, including all the structural types computed with our original force field). The force constants k_θ are given in *Table 1* (force-field parameters not given in *Table 1* have been published in [3b] [13] [14]). Selected examples showing

Table 1. *Force Constants* k_θ *for the Harmonic sine Function* $E_\theta = 1/8\, k_\theta \sin^2(2\theta)$ [a])

Metal centre	Ligand atoms		k_θ [mdyn Å][b])	Metal centre	Ligand atoms		k_θ [mdyn Å][b])
Ti⁴⁺	X^c)	X^c)	0.000	Cu²⁺	N^d)^c)^h)	N^d)^e)^h)	0.013
Cr³⁺	N^d)^e)	N^d)^e)	0.025		N^d)^e)^h)	O^f)^j)^k)	0.007
Fe³⁺ (low-spin)	N^d)^e)	N^d)^e)	0.042		N^d)^e)^h)	S^l)	0.013
Co³⁺	N^d)^e)	N^d)^e)	0.050		S^l)	S^l)	0.013
	N^d)^e)	O^f)^g)	0.045		O^f)^j)^k)	O^f)^j)^k)	0.002
	O^f)^g)	O^f)^g)	0.040		O^f)^j)^k)	S^l)	0.007
Co²⁺	N^e)	N^e)	0.023	Zn²⁺	X^c)	X^c)	0.000
	N^d)	N^d)	0.017	(octahedral,			
Ni²⁺	N^d)^c)	N^d)^e)	0.025	tetrahedral)			
	N^d)^e)	O^f)	0.026				
	O^f)	O^f)	0.027				

[a]) Parameters not given in our published force field [3b] [13] [14] are: Co^II–N(amine): $k = 0.600$ mdyn/Å, $r_0 = 2.140$ Å; Co^III–N(pyridine): $k = 0.820$ mdyn/Å, $r_0 = 2.100$ Å; Zn^II(tetrahedral)–N(amine): $k = 0.350$ mdyn/Å, $r_0 = 2.060$ Å.

[b]) The conversion factor to kJ/mol is 602.2.

[c]) Independent of the ligand atom.

[d]) Amine.

[e]) Pyridine.

[f]) Carboxylate.

[g]) β-Diketonate.

[h]) Amide.

[i]) Nitro.

[k]) Water.

[l]) Thiaether.

Table 2. *Comparison of the Original* [3b] *and the 'Electronically Doped' Force Fields Based on Some Selected Examples*

Compound[a])	Parameter[b]) [°]	X-Ray	Original force field	'Electronically doped' force field
[Cr^III(tn)₃]³⁺	ϕ	59 [15]	48	54
[Co^III(tmen)₃]³⁺	ϕ	44 [16]	41	44
[Ni^II(tn)₃]²⁺	α	174 [17]	166	173
[Cu^II((R)-ahaz)((S)-ahaz)]²⁺	θ	0 [18]	8	0

[a]) tmen = 2,3-dimethylbutane-2,3-diamine, tn = propane-1,3-diamine, ahaz = 2-azacycloheptanamine.

[b]) ϕ = trigonal twist angle (octahedral, $\phi = 60°$; trigonal prismatic, $\phi = 0°$); α = *trans* angle; θ = tetrahedral twist angle (tetrahedral, $\theta = 90°$; square planar, $\theta = 0°$).

Table 3. *Improvement of the Accuracy of the Calculated Structures of Transition-Metal Complexes with the 'Electronically Doped' Force Field*

Metal-ligand distance r

	X-Ray *vs.* original force field [3b]		X-Ray *vs.* 'electronically doped' force field	
	Average deviation	Maximum deviation	Average deviation	Maximum deviation
Cr³⁺	0.002	0.035	0.002	0.029
Fe³⁺	0.002	0.004	0.002	0.005
Co³⁺	0.007	0.045	0.007	0.038
Co²⁺	0.012	0.080	0.020	0.069
Ni²⁺	0.004	0.029	0.004	0.026
Cu²⁺ ^a)^b)	0.008	0.027	0.009	0.026

Table 3 (cont.)

Trigonal twist angles ϕ

	X-Ray *vs.* original force field [3b]		X-Ray *vs.* 'electronically doped' force field	
	Average deviation	Maximum deviation	Average deviation	Maximum deviation
Cr^{3+}	7	11	4	6
Fe^{3+}	2	6	3	5
Co^{3-}	1	3	0	2
Co^{2-}	10	13	10	12
Ni^{2+}	4	11	2	4
$Cu^{2+\,a})$	5	9	5	13

rms Values of the chromophores

	X-Ray *vs.* original force field [3b]	X-Ray *vs.* 'electronically doped' force field
Ti^{4+}	0.18	$-^{c})$
Cr^{3+}	0.11	0.09
Fe^{3+}	0.07	0.07
Co^{3+}	0.07	0.06
Co^{2+}	0.16	0.14
Ni^{2+}	0.11	0.08
Cu^{2-}	0.18	0.16
Zn^{2+} (octahedral)	0.60	$-^{c})$
Zn^{2+} (tetrahedral)	0.03	$-^{c})$

^{a})   Axial bond distances are, due to *Jahn-Teller* distortions, less accurate [19].
^{b})   Only equatorial bonds considered.
^{c}) $k_{LML'} = 0$.

the enhancement of the accuracy of calculated structures using the electronically doped force field are presented in *Table 2*, and *Table 3* summarizes the mean improvement with all 52 structures considered here (tables with the complete structural data (X-ray, original force field [3b], electronically doped force field are available as supplementary material).

The force constants k_{θ} (*Table 1*) are about an order of magnitude smaller than those used in force fields that do not include 1,3-nonbonded interactions. This is not unexpected, since the angle term is introduced here to a force field based on 1,3-nonbonded interactions that already lead to rather accurate computed structures. Thus, it is a small perturbation and, in this respect, similar to a bond angle-bond length cross-term.

The perturbation with the ligand-field term generally leads to a small improvement of the accuracy of the computed structures. Some of the most impressive improvements are shown in *Table 2*. However, in most cases the correction by the harmonic sine potential is rather small and, in view of the expected accuracy of structural predictions by empirical force-field calculations, close to irrelevant. It is important, however, that *i*) we did not find any example, so far, where the addition of the electronic perturbation leads to appreciably less accurate results, and *ii*) there are, albeit, few cases where the electronic perturbation leads to a considerable improvement. This is especially relevant for chromophores with rather large ligand fields and relatively long metal–ligand bonds (for short metal–ligand distances which usually are in parallel with strong ligand fields, the 1,3-repulsive terms are dictating octahedral geometry, *e.g.* 90° angles). Therefore, the

Table 4. *Improved Accuracy of Calculated Spectroscopic Properties (MM-AOM)*[a])

Compound	Obs. transition [cm^{-1}]	Calc. transition (original force field)[b])[c]) [cm^{-1}]	Calc. transition ('electronically doped' force field) [cm^{-1}]
[Cr^{III}(dtne)]$^{3+}$	20790	20250	20431
[Cr^{III}(*mer*-dtn)$_2$]$^{3+}$	21100	20050	20362
[Cr^{III}(*cis*-cyclam)(NH$_3$)$_2$]$^{3+}$	21380	21610	21515
[Cr^{III}(*tea*-tacn)]$^{3+}$	21410	21990	21361
[Cr^{III}(tn)$_3$]$^{3+}$	21570	21190	21416
[Cr^{III}(*mer*-dien)$_2$]$^{3+}$	21700	21360	21727
[Cr^{III}(NH$_3$)$_6$]$^{3+}$	21640	21420	21529
[Cr^{III}(en)$_3$]$^{3+}$	21800	21780	21873
[Cr^{III}(*cis*-diammac)]$^{3+}$	22120	21790	22124
[Cr^{III}(sar)]$^{3+}$	22180	22515	21763
[Cr^{III}(*sym-fac*-dien)$_2$]$^{3+}$	22170	22110	22092
[Cr^{III}(tacn)$_2$]$^{3+}$	22780	23120	23045
[Cr^{III}(*trans*-cyclam)(NH$_3$)$_2$]$^{3+}$	23140	23045	23905
[Cr^{III}(*trans*-diammac)]$^{3+}$	23420	23525	23467
[Ni^{II}(NH$_3$)$_6$]$^{2+}$	10750	10661	10639
	17500	17170	17026
[Ni^{II}(tn)$_3$]$^{2+}$	10900	10555	10933
	17800	17698	17625.
[Ni^{II}(*mer*-dtn)$_2$]$^{2+}$	10970	11879	10312
	17570	16915	16733
[Ni^{II}(*mer*-dien)$_2$]$^{2+}$	11500	11898	11537
	18700	20371	18587
[Ni^{II}(tach)$_2$]$^{2+}$	11550	11610	11602
	18850	18424	18406
[Ni^{II}(en)$_3$]$^{2+}$	11700	11952	11953
	18350	17953	18362
[Ni^{II}(*trans*-diammac)]$^{2+}$	12845	11981	12879
	20500	20666	20421

[a])   Included are Cr^{III}- and Ni^{II}-hexaamines from our previous work; for ligand abbreviations and references for the experimental spectra see [9]; for simplicity only one transition is given for Cr^{III} (^{4}A$_{2g}$ → ^{4}T$_{2g}$, in O_h), and two are reported for Ni^{II} (^{3}A$_g$ → ^{1}E$_g$, ^{3}A$_g$ → ^{3}T$_{2g}$, in O_h).
[b])   [3b].
[c])   The values reported for Ni^{II} differ from those published before [9] since here we use the original parameters [3b] for 1,3-nonbonded interactions (see [9] and text).

most relevant examples for improved structural accuracies are those of Cr^{III} and Ni^{II} complexes with relatively flexible ligand systems. The relevance of the improved accuracy is best demonstrated with the calculations of electronic ground and excited states by AOM calculations, derived from structures estimated by molecular mechanics, to compute spectroscopic properties (MM-AOM) [8–11]. The examples presented in *Table 4*, including the previously published examples, demonstrate how important an accurate prediction of the angular geometry is. In our original publication, good agreement between calculated and observed spectra for Ni^{II} complexes was only possible with a modification of the *van der Waals* parameters [9]. The approach presented here is more elegant and generally applicable, it does not increase the computational expense, and, therefore, it is considerably more satisfactory.

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