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# Simulation of Plasticity of Copper(II) Coordination Polyhedron by Means of an Empirical Force Field Method

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The empirical force field method of conformational analysis was used in order to reproduce the distorted planar geometry of bis-(*N*-alkylsalicylaldiminato) copper(II) complexes. The problem was partly solved by introducing two apically bonded »dummy« atoms. The parameters adjusted to reproduce the configuration of copper atom in the orthorhombic modification of ethylated derivative, were shown to be adequate for the calculation of epimer-selectivity effect in epimeric (M(L-ligand) (L-ligand) and M(L-ligand) (D-ligand)) copper(II) complexes with *N,N*-dimethylvaline. Calculations on other, more distorted structures of *N*-substituted copper(II) bis-salicylaldiminates (substituents: ethyl, t-butyl and i-propyl) were not able to reproduce crystal geometries suggesting that the model is applicable only for small deviations from planarity.

## INTRODUCTION

In our previous papers on the estimation of the diastereoselectivity effect (difference in thermodynamic stability between M(L-ligand) (L-ligand) and M(L-ligand) (D-ligand) complexes) in copper(II) bis-complexes with *N,N*-dimethylvaline[1] and *N,N*-dimethylisoleucine[2] our computed values for the diastereoselectivity effect were systematically higher than those obtained experimentally[3]. This disagreement between theory and experiment was suggested to be primarily caused by an improper simulation of interactions in the coordination polyhedron, i. e. that too strong a potential holding the ligand atoms in an »idealized« (planar) configuration had been chosen[1].

This is not surprising because in our previous work, we were using the parameters for octahedral cobalt(III) complexes neglecting the fact that copper(II) coordination sphere shows a considerable plasticity[4] which results in a very pronounced distorsion isomerism[5] (in our »dummy« ligand atom model[6] approximately planar complexes are represented as being octahedrally coordinated, by introducing two apically coordinated »dummy« ligand atoms simultating the two lone electron pairs). Therefore we decided to test our »dummy« atom model on the classical problem of an intermediate (between planar and tetrahedral) configuration of copper(II) bis-complexes with *N*-alkylsalicylaldiminates. The main aim of our investigations was to obtain such a set of empirical parameters which would be suitable not only for reproducing the crystal geometries but also for estimating the diastereoselectivity effect in copper(II) complexes. This attempt to calculate as many observables as possible from the given set of empirical parameters is in accordance with basic philosophy of the consistent force field (CFF) approach[7,8].

## METHODS

Conformational (strain) energy was calculated from the basic formula:

$$V = \frac{1}{2} \sum_i k_{b,i} (b_i - b_{0,i})^2 + \frac{1}{2} \sum_j k_{\Theta,j} (\Theta_j - \Theta_{0,j})^2 + \frac{1}{2} \sum_k V_{n,k} (1 \pm \cos n\phi) + \sum_l A_l \exp(-B_l r_l) - C_l r_l^{-6} \tag{1}$$

in which $b$, $\Theta$, and $\phi$ stand for bond lengths, valence and torsional angles, respectively; r is the non-bonded distance, $k_b$ is the empirical parameter for bond stretching, and $k_\Theta$ is the parameter for valence angle bending. Torsional interactions were determined with parameters $V_n$ and $n$ (height and multiplicity of the torsional barrier, respectively), and non-bonded interactions were computed from Buckingham function with parameters $A$, $B$ and $C$. The parameters are the same as published previously[4], except the new ones which are presented in Table I. The conformational calculations were performed with the program developed by S. R. Niketić and Kj. Rasmussen[8].

The average Gibbs energy of an epimer was calculated from the formula:

$$G = \sum_i G_i w_i / \sum w_i \tag{2}$$

where $G_i$ denotes the Gibbs energy of i-th conformer; the conformer »weights« $w_i$ were calculated from the Boltzmann formula: $w_i = \exp(-G_i/RT)$. The methods for calculating the approximate value of formula (2) can be found elsewhere[2].

Root-mean-square deviations were calculated from the formula:

$$\varepsilon_{\mathrm{r.m.s.}} = \sqrt{\frac{1}{6} \sum_{i=1}^{6} (\Theta_i - \Theta_{i,o})^2} \tag{3}$$

where $\Theta_i$ and $\Theta_{i,o}$ denote the values of the relevant valence angles (O—M—O, O—M—N or N—M—N) obtained from conformational analysis calculations (or from an idealized model) and crystal structure, respectively.

## RESULTS AND DISCUSSION

For the calculation of stable conformations of bis-($N$-alkylsalicylaldiminato)copper(II) complexes we used two sets of empirical parameters (see Table I): an asymmetrical force field (FF2) and a symmetrical force field (FF3). In the asymmetrical force field we used the previously published parameters[4] for valence angle bending of copper-ligand valence angles, and varied the valence angle bending parameters for »dummy« atoms; in the symmetrical force field we varied all valence angle bending parameters with the central atom (taking them to be equal to each other).

The minimized crystal structure of the orthorhombic form of bis-($N$-ethylsalicylaldiminato)copper(II) showed, for widely varying values for angle bending parameters, a very good agreement with the crystal structure geometry[9] of the coordination polyhedron (see Figure 1). Unfortunately, the rest of the investigated crystal structures did not show such a good agreement: the monoclinic ethylated complex[10] showed a steady increase in $\varepsilon_{\mathrm{r.m.s}}$ value

TABLE I

*Empirical Force Field Parameters Used for Minimization of Crystals Structures of Bis-(N-alkylsalicylaldiminato) Copper(II) Complexes*[a]

*Bond stretching*

| Bond | $k_b$/(kcal mol$^{-1}$ Å$^{-2}$ | $b_o$/Å |
|---|---|---|
| K—K | 719.0 | 1.40 |
| K—H | 719.0 | 1.085 |
| N—K | 862.8 | 1.307 |
| K—Q | 100.0 | 1.0 |

*Angle bending*

| Angle | $k_\Theta$/(kcal mol$^{-1}$ rad$^{-2}$) | $\Theta_o$/rad |
|---|---|---|
| N—M—O | 97.784 (11.0)[b] | 1.571 |
| X—M—N | 9.0 (11.0)[b] | 1.571 |
| X—M—O | 9.0 (11.0)[b] | 1.571 |
| M—N—K | 57.52 | 2.094 |
| A—K—B | 143.8 | 2.094 |
| K—N—C | 80.0 | 2.094 |
| K—K—O | 143.8 | 2.094 |
| C—N—C[c] | 143.8 | 1.911 |

*Torsional potential*

| Angle | $V_n$/(kcal mol$^{-1}$) | $n$ |
|---|---|---|
| O—M—N—C | 5.0 | —2 |
| N—M—O—K | 5.0 | —2 |
| M—O—K—K | 5.0 | —2 |
| N—K—K—K | 5.0 | —2 |
| M—N—K—K | 5.0 | —2 |

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[a] Other parameters are the same as in Ref. 4. Uncommon symbols: A, B, any atom defining the valence angle; X, »dummy« ligand atom; Q, »dummy« atom representing the carbon atom in omitted aromatic ring; K, planar carbon atom; M, copper(II).

[b] Value for symmetric force field.

[c] Value for conformational calculation on copper(II) *N,N*-dimethylvalinates.

with increasing $k_\theta$ while for *t*-butyl[11] and *i*-propyl[12] derivatives very high (about 13°) values of $\varepsilon_{r.m.s}$ were obtained. These values were not very sensitive to the changes in the parameter $k_\theta$. It must be noted, however, that the orthorhombic modification of bis-(*N*-ethylsalicylaldiminato) copper(II) has the least distorted structure among all the investigated complexes. The deviation from planarity — measured as $\varepsilon_{r.m.s}$ deviation between the relevant valence angles of crystal and »idealized«, i. e. strictly planar structure — of that complex is by far the least of all investigated structures (4.29°, compared with 15.17°, 23.08° and 25.68° for monoclinic modification and *t*-butyl and *i*-propyl derivatives, respectively).

We used the newly developed parameters for valence angle bending potential to perform a conformational analysis of MLL and MDL isomers of bis-(*N,N*-dimethylvalinato) copper(II), minimizing only 10 (of altogether 21) lowest conformations (see Table II). Both force fields (FF2 and FF3) yielded the values of epimer-selectivity effect ($\Delta_r G_{LL} - \Delta_r G_{DL}$) virtually within the error-limits of the experimentally obtained value (2.95 kJ mol$^{-1}$ and 4.39 kJ mol$^{-1}$ for FF2 and FF3, respectively, compared with the experimental value[3] 2.9 . . . 4.0 kJ mol$^{-1}$). Comparing these results with the previously published

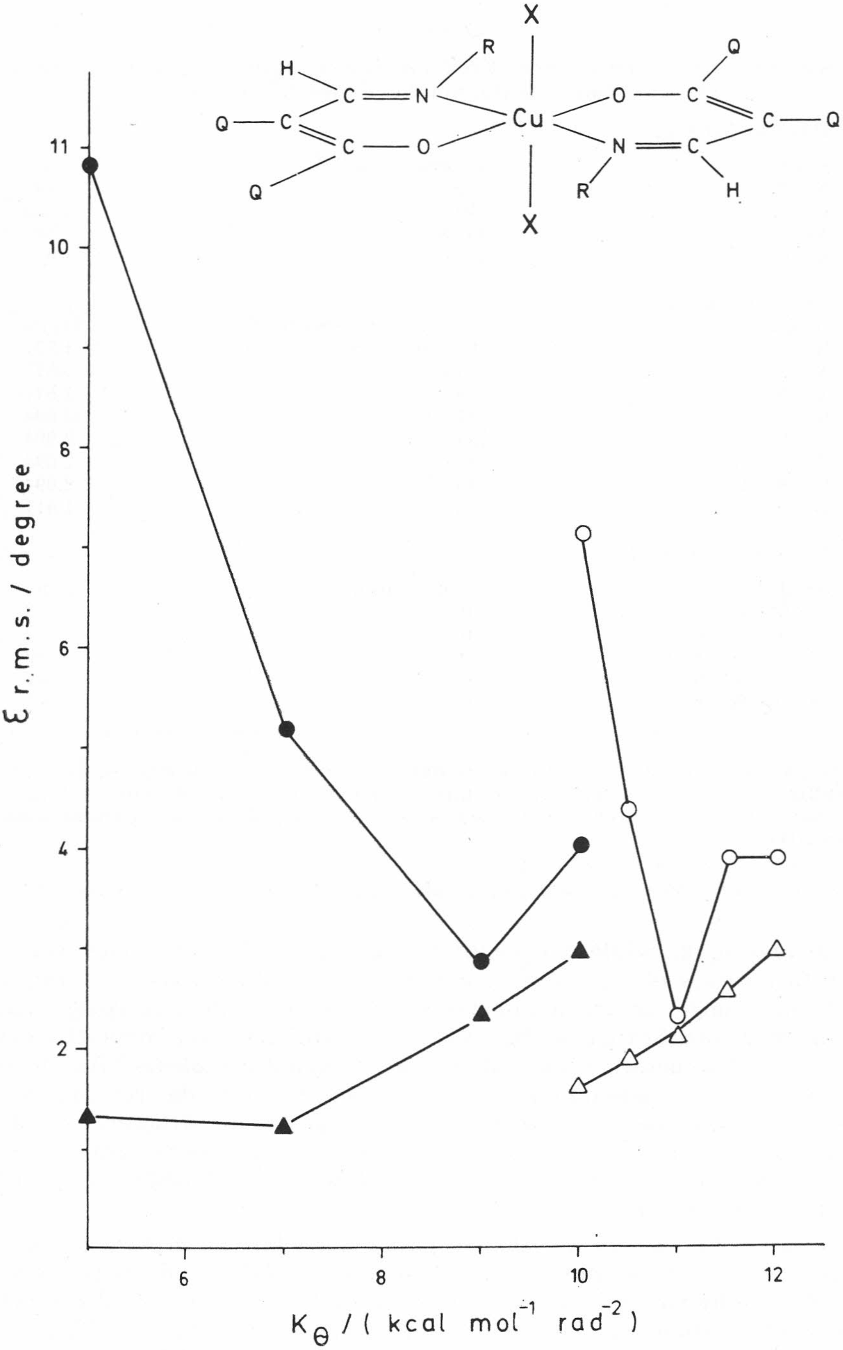

Figure 1. The reproducibility of the planar configuration ($\varepsilon_{\mathrm{r.m.s.}}$, see Methods) as a function of parameter $k_{\Theta}$ ($k = k_{\mathrm{X-M-N}} = k_{\mathrm{X-M-O}}$, Eq. 1): orthorhombic (○) and monoclinic (△) modification of *bis*-(*N*-ethylsalicylaldiminato)copper(II); the hollow symbols refer to calculations with symmetrical force field and the filled ones to calculations with the asymmetrical force field. Formula: Q and X denote dummy atoms simulating the phenyl group and the lone electron pair on copper(II) atom, respectively, R = Et.

TABLE II

*Comparison of Three Force Fields*[a] *for the Estimation of Gibbs Energy and Statistical Weights of the Conformers of Two Isomers of* Bis-(N,N-*dimethylvalinato)copper(II)*[b]

| No.[c] | *FF1*[d] LL-isomer | *FF1*[d] DL-isomer | *FF1*[d] Δ G | *FF2*[d] LL-isomer | *FF2*[d] DL-isomer | *FF2*[d] Δ G | *FF3*[d] LL-isomer | *FF3*[d] DL-isomer | *FF3*[d] Δ G |
|---|---|---|---|---|---|---|---|---|---|
| 1—3 | 22.46 | 22.96 | —0.50 | 24.91 | 26.57 | —1.66 | 25.10 | 26.56 | —1.46 |
| 1—6 | 5.40<br>(0.079) | 4.59<br>(0.005) | 0.81 | 10.74<br>(0.012) | 9.77<br>(0.006) | 0.97 | 9.77<br>(0.017) | 9.37<br>(0.019) | 0.40 |
| 2—6 | 16.19 | 16.24 | 0.66 | 22.20 | 21.36 | 0.84 | 21.50 | 21.15 | 0.35 |
| 3—3 | 26.07 | 26.93 | —0.86 | 26.21 | 29.45 | —3.24 | 26.90 | 31.07 | —4.17 |
| 3—4 | 19.50 | 19.50 | 0.00 | 23.22 | 21.17 | 2.05 | 21.90 | 21.33 | 0.57 |
| 3—6 | 8.21<br>(0.026) | 8.00<br>(0.001) | 0.21 | 13.41<br>(0.004) | 12.23<br>(0.002) | 1.18 | 12.35<br>(0.006) | 12.18<br>(0.001) | 0.17 |
| 4—6 | 3.07<br>(0.201) | 2.31<br>(0.014) | 0.76 | 7.16<br>(0.052) | 6.67<br>(0.022) | 0.49 | 5.98<br>(0.080) | 5.84<br>(0.019) | 0.14 |
| 5—5 | 30.44 | 22.34 | 8.10 | 29.24 | 26.61 | 2.63 | 28.64 | 24.48 | 4.18 |
| 5—6 | 15.23<br>(0.002) | 7.01<br>(0.002) | 8.22 | 14.65<br>(0.003) | 12.40<br>(0.002) | 2.25 | 14.28<br>(0.003) | 10.58<br>(0.003) | 3.70 |
| 6—6 | 0.00<br>(0.689) | —8.37<br>(0.977) | 8.37 | 0.00<br>(0.929) | 2.70<br>(0.967) | 2.70 | 0.00<br>(0.893) | —3.92<br>(0.972) | 3.92 |
| Estimated epimer-selectivity: |  |  | 9.47 |  |  | 2.95 |  |  | 4.39 |
| Experimental value[3]: |  |  |  | 2.9 . . . 4.0 |  |  |  |  |  |

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[a] *FF1:* force field from a previous paper[1]; *FF2:* asymmetric force field; *FF3:* symmetric force field (see text).

[b] All Gibbs energies are given in kJ $mol^{-1}$, as calculated at $T = 298.16$ K. Statistical weights greater than 0.0009 are given in parentheses.

[c] The conformers are designed as a combination of the conformers of the constituting chelate rings. The energies and geometries of six basic conformations of (*N,N*-dimethylvalinato)copper(II) chelate ring were given elsewhere[1].

[d] Zero points: 1084.76 kJ $mol^{-1}$ for *FF1*, 1061.91 kJ $mol^{-1}$ for *FF2*, and 1055.67 kJ $mol^{-1}$ for *FF3*.

ones[1], we noted that the newly developed force fields tended to give a greater abundance of the lowest minimum (cf. 6—6, Table II) but also, to some degree, they gave a wider distribution of the stereoselective effect among the conformers.

In spite of neglecting the intermolecular interactions in the crystal lattice and the use of nonoptimized parameters, our results suggest that the »dummy« ligand atom model is a useful tool for conformational analysis, at least for weakly distorted planar copper(II) complexes.

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## SAŽETAK

### Simulacija plastičnosti koordinacijskog poliedra dvovaljanog bakra metodom empirijskog polja sila

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Pokušalo se metodom empirijskog polja sila reproducirati distordiranu planarnu geometriju bis-kompleksa bakra s *N*-alkilsalicilaldiminatima. Problem je djelomično riješen uvođenjem dvaju apikalno vezanih »lažnih« atoma (liganada). Parametrima koji su ugođeni tako da reproduciraju konfiguraciju bakrova atoma u ortorompskoj modifikaciji etilnog derivata mogao se, gotovo u granicama eksperimentalne točnosti, izračunati i epimer-selektivni efekt u epimernim kompleksima — M(L-ligand) (L-ligand) i M(L-ligand) (D-ligand) — bakra s *N,N*-dimetilvalinom. Kristalne geometrije drugih, jače distordiranih struktura *N*-supstituiranih bakrovih bis-salicilaldiminata (supstituenti: etil, butil, *i*-propil) nisu se mogle reproducirati, što pokazuje da je model pogodan samo kada su devijacije od planarnosti malene.