

CCA-1879

YU ISSN 0011-1643

UDC 541.61; 548.736

Original Scientific Paper

Simulation of Plasticity of Copper(II) Coordination Polyhedron: Empirical Force Field Model with Distorsion Coordinate Potential

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Received September 12, 1988

In order to reproduce the geometry of tetracoordinated copper(II) chelates with a »distorted« coordination polyhedron (planar/tetrahedral), two new empirical functions for the calculation of the conformational potential were introduced. The first depends on the distorsion coordinate β , defined as an angle between bisectors of two valence angles around the central atom. The second function is a two-well valence angle bending potential for valence angles around copper, with minima at 90° and 109.47° .

The new functions were tested on bis-(*N,N*-dimethylvalinato)-copper(II). A consistent force field (CFF) calculation with the new functions yielded the correct geometry of copper coordination, i. e. a distorted tetrahedron. The valence angles around copper (N—Cu—N, O—Cu—N and O—Cu—O) were reproduced fairly well with root-mean square deviation with respect to the crystal structure of 3.20° and 3.73° for the model with a two-well and the model with a quadratic valence angle bending potential, respectively. The measured diastereoselectivity (Gibbs energy difference between Cu(L-ligand)₂ and Cu(L-ligand)(D-ligand)) was reproduced within 3 kJ mol⁻¹.

INTRODUCTION

A well known property of copper(II) complexes is the plasticity of their coordination sphere^{1,2}. This means that they do not usually form »regular« (planar or tetrahedral) coordination polyhedra. The phenomenon can be manifested both geometrically (structurally) and thermodynamically. Copper coordination geometry strongly depends on both the bonded and non-bonded interactions; therefore, some copper complexes can form crystal modifications differing in coordination geometry (distorsion isomerism³). In addition to these structural effects, the plasticity of the coordination sphere causes a weakening of the diastereoselectivity effects* in copper chelates in comparison

* Defined as $\Delta G = -RT \ln(\beta_{MLL}/\beta_{MDL})$, L and D denoting ligand enantiomers and β cumulative stability constants.

with complexes having more rigid coordination (e. g. cobalt and nickel(II) complexes⁴).

Our principal aim is to develop a force field (i. e. empirical functions for conformational or strain energy) which should reproduce both the structural and thermodynamical properties of copper(II) chelates, as well as properties of other metal chelates with non-rigid coordination. Our first attempt to estimate the diastereoselectivity effect in copper(II) complexes with *N*-alkylated amino acids⁵ demonstrated too big a difference in energy between MLL and MDL complexes of *N,N*-dimethylvaline. This discrepancy, which was later shown to hold true also for a similar complex, bis-(*N,N*-dimethylisoleucinato)copper(II)⁶, was attributed to the fact that the parameters holding ligand atoms in plane were too strong^{5,7}. This is not very surprising because we used the same empirical parameters as for more rigid cobalt(III) and chromium(III) complexes^{8,11}. In our first attempt to simulate the geometry of tetracoordinated copper(II) complexes we added two apically placed »dummy« atoms to hold copper and ligand atoms in plane (»dummy« atom model)⁹. »Softening« the force field, i. e. putting the smaller values for angle bending, k_{θ} , parameters around copper, gave acceptable results with respect to energy⁷, but wrong results with respect to geometry: attempts to reproduce the crystal geometry of bis-(*L-N,N*-dimethylvalinato)copper(II)** coordination polyhedron yielded a distorted pyramid instead of a distorted tetrahedron¹⁰.

To achieve a better reproduction of copper(II) coordination geometry, we have introduced a new empirical potential depending on distortion angle β (Figure 1). Angle β remains unchanged during the transition from planar to tetrahedral coordination and it causes an additional strain in the molecule for pyramidal distortion. Therefore, the new models (denoted as Model 1 and Model 2) based on that potential would yield tetrahedral distortion instead of the pyramidal one.

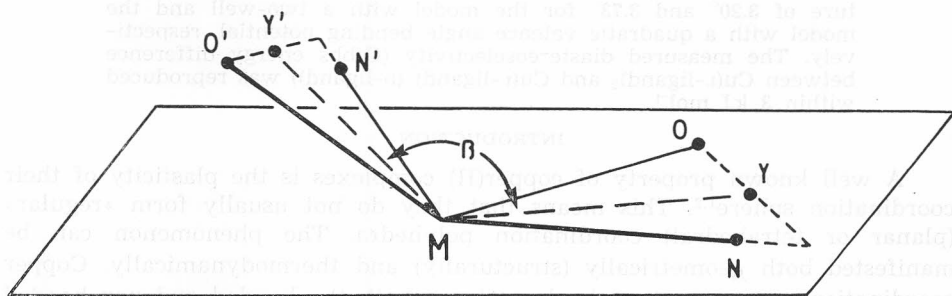


Figure 1. Distortion angle β is defined as an angle between the bisectors of angles OMN and O'MN' (M denotes the central atom), Y and Y' are »dummy« atoms needed in constructing the angle.

** *N,N*-dimethylvaline: *N,N*-dimethyl-3-methyl-2-aminobuthanoic acid.

METHODS

The conformational (strain) potential energy was calculated from the basic formula:

$$V = (1/2) \sum_i k_{b,i} (b_i - b_{0,i})^2 + 1/2 \sum_j k_{\theta,j} (\theta_j - \theta_{0,j})^2 + 1/2 \sum_k V_n (1 \pm \cos n \varphi_k) + \\ + \sum_1 (A_1 \exp(-B_1 r_1) - C_1 r_1^{-6}) + 1/2 \sum_m k_{\chi,m} \chi_m^2 + 1/2 k_{\beta} (\beta - \beta_0)^2 + V_{NMO} \quad (1)$$

in which b , θ , φ and χ stand for bond lengths, valence, torsional and out-of-plane angles, respectively; r is non-bonded distance, k_b is an empirical parameter for bond stretching and k_{θ} for valence angle bending. Torsional interactions were determined with parameters V_n and n (height and multiplicity of torsional barrier, respectively) and non-bonded interactions were computed from a Buckingham function with parameters A , B and C . In addition, the out-of-plane deformation potential for the carboxyl group with quadratic function dependent on parameter k_{χ} and distortion potential (parameters k_{β} and β_0) was also computed. The last term in equation (1) is angle-bending potential for angles N—Cu—O which can be quadratic:

$$V_{NMO} = (1/2) k_{\theta} (\theta - \theta_0)^2 \quad (2)$$

(Model 1) or in the form of cosine power series (Model 2), see below. Model 1 has a minimum for N—Cu—O angles only at $\theta = 90^\circ$ (planar configuration). Conversely, Model 2 has two minima for N—Cu—O angles which correspond to planar ($\theta_{01} = 90^\circ$) and tetrahedral ($\theta_{02} = 109.47^\circ$) configurations. Therefore, with Model 2 both configurations of copper coordinations (planar and tetrahedral) are possible.

The parameters were the same as those used in our first paper⁹ with the exception of C—N—C bending parameters which were taken to be equal to the parameters for C—C—C bending. Parameters for the valence angle bending around the copper atom (angles N—Cu—O) and those for distortion angle potential were determined separately (see Results and Discussion). Empirical constant k_{χ} was taken to be 100 kcal mol⁻¹ rad⁻². Calculations were performed by the program developed by Kj. Rasmussen and co-workers^{11,12} which was further modified to cope with new empirical potentials.

Distorsion angle (Figure 1) is calculated as a »valence« angle Y—M—Y', where Y and Y' are »dummy« atoms placed on the bisector of angles O'MN and O'MN', respectively, and M is the central (copper) atom.

The coordinates of »dummy« atom Y are taken to be:

$$x_{iY} = (1/2) (x_{iO} + a x_{iN}) \quad i = 1 \dots 3 \quad (3)$$

where x_{iO} and x_{iN} are cartesian coordinates of O and N atoms (origin of the frame is the central atom M). Variable a is defined as:

$$a = b_{MO}/b_{MN} \quad (4)$$

where x_{iO} and x_{iN} are cartesian coordinates of O and N atoms (origin of atom Y' the variables $x_{iY'}$ and a' are defined in the same way).

Denoting by l and l' the lengths of the »bonds« $M-Y$ and $M-Y'$, the distortion angle β can be expressed as:

$$\cos \beta = \frac{\sum_{i=1}^3 x_{iY} x_{iY'}}{ll'} \quad (5)$$

Such a formulation of the distortion angle enables us to use the existing subroutines in our conformational program for calculating energies and their differentials with respect to valence angles.

Two-well angle bending potential for the NMO angles (Model 2) was calculated from the polynomial function of the general form:

$$V_z = a z^4 + b z^3 + c z^2 + d z + e \quad (6)$$

where $z = \cos \theta$. Choosing parameters a , b , c , d , and e so that function (6) has two minima ($\theta_{o1} = 90^\circ$, $\theta_{o2} = 109.47^\circ$) and satisfies the conditions $V(0) = 0$ and $d^2 V_z/dz^2|_{\theta=\theta_{o1}} = k_z > 0$, the equation (6) can be rewritten in the form:

$$V_z = 9/2 (k_z - 54h) z^4 + 3 (k_z - 36h) z^3 + 1/2 k_z z^2 \quad (7)$$

where h is the difference in energy between two minima and k_z is an empirical parameter.

Function (7) has a maximum at a point:

$$z_{\max} = \frac{-k_z}{6(k_z - 54h)} \quad (8)$$

If both minima have the same energy (i. e. $h = 0$), line $z = z_{\max}$ should be the symmetry axis of function (7).

Root-mean-square deviation between crystal and theoretical structures was calculated from:

$$\varepsilon_{r.m.s.}(\Delta X) = (1/N \sum_{i=1}^N (\Delta X_i)^2)^{1/2} \quad (9)$$

where X stands for the angles around copper (valence angles, θ , distortion angle β and »torsional angle« φ (ONN'O')) when comparing the copper coordination geometry, or for interatomic distance, r , when checking the overall similarity. Mark Δ denotes the difference between the values of the observable X in two structures.

The average Gibbs energy of a diastereomer (MLL or MDL) was calculated from the formula:

$$\langle G \rangle = \sum w_i G_i / \sum w_i \quad (10)$$

where G_i denotes the Gibbs energy of the i -th conformer, and w_i stands for the statistical weight calculated from the Boltzmann formula. Details of calculations were given elsewhere⁹.

RESULTS AND DISCUSSION

In order to test our new models (Model 1 and Model 2), we tried to reproduce both the crystal geometry¹⁰ and the observed diastereoselectivity (enantioselectivity)¹³ of bis-(N,N -dimethylvalinato)copper(II). The most critical

parameters (k_{NMO} , k_z and k_β) were varied until the best agreement (expressed as $\epsilon_{\text{r.m.s.}}(\Delta\theta, \Delta\beta, \Delta\varphi)$) was obtained (footnote to Table III). Both models yielded the best agreement for $k_\beta = 37.5 \text{ kcal mol}^{-1} \text{ rad}^{-2}$ showing almost the same values of r.m.s. deviation (Table I).

TABLE I

*Comparison of the Experimental and Theoretical Geometry of the Coordination Polyhedron of Bis-(L-N,N-dimethylvalinato)copper(II)**

Angle	Crystal Structure	Model 1	Difference Experimental -theoretical	Model 2	Difference Experimental -theoretical
N—Cu—N'	161.45	159.90	1.55	160.10	1.35
N—Cu—O	84.32	88.41	-4.09	89.10	-4.78
N—Cu—O'	97.07	92.68	4.39	91.90	5.17
N'—Cu—O	95.30	92.68	2.62	91.90	3.40
N'—Cu—O'	84.75	88.41	-3.66	89.10	-4.35
O—Cu—O'	175.51	173.78	1.73	174.22	1.29
φ (ONN'O')	-156.14	-153.74	-2.40	-154.36	-1.78
β	170.49	170.38	0.11	170.15	0.34
$\epsilon_{\text{r.m.s.}}(\Delta\theta)$		3.20		3.73	
$\epsilon_{\text{r.m.s.}}(\Delta\theta, \Delta\beta, \Delta\varphi)$		2.90		3.29	

* All values are expressed in $^\circ$. For definition of models see Methods.

Both theoretical structures had the correct geometry of a copper coordination polyhedron (i. e. a distorted tetrahedron) which was not possible to obtain with the »dummy« atom model (Figure 2), but the checking of the overall similarity (expressed as $\epsilon_{\text{r.m.s.}}(\Delta r)$) between the crystal and theoretical structures (Table II) yielded essentially the same results for all models.

The conformation of one of the chelate rings (Ring 2) was better reproduced than that of the other, Ring 1 (for the definition of the rings see Figure 3). Even the values of $\epsilon_{\text{r.m.s.}}(\Delta r)$ were almost the same: 0.087 Å (Model 1) and 0.089 Å (Model 2) for Ring 1 (0.085 Å, »dummy« atom model¹⁰) and 0.059 Å

TABLE II

*Comparison of the Experimental and Theoretical Structure of Bis-(L-N,N-dimethylvalinato)copper(II)**

	$\epsilon_{\text{r.m.s.}}(\Delta r)/\text{Å}$			
	Crystal structure Ring 2	Model 1 Ring 1	Model 1 Ring 2	Model 2 Ring 1 Ring 2
Crystal Structure		0.1410		0.1475
Ring 1	0.0732	0.0871	0.0872	0.0892 0.0893
Ring 2		0.0585	0.0588	0.0608 0.0611
Model 1				0.1112
Ring 1			0.0010	0.0049 0.0049
Ring 2				0.0050 0.0049
Model 2				
Ring 1				0.0010

* Only non-hydrogen atoms are taken into account. Theoretical structures correspond to minimum 6-6LL (Table III, IV).

(Model 1) and 0.061 Å «Model 2) for Ring 2 (0.053 Å, »dummy« atom model¹⁰). The overall similarity between the whole molecular crystal and the theoretical structures (Table II and Figure 3) is also comparable with the results obtained

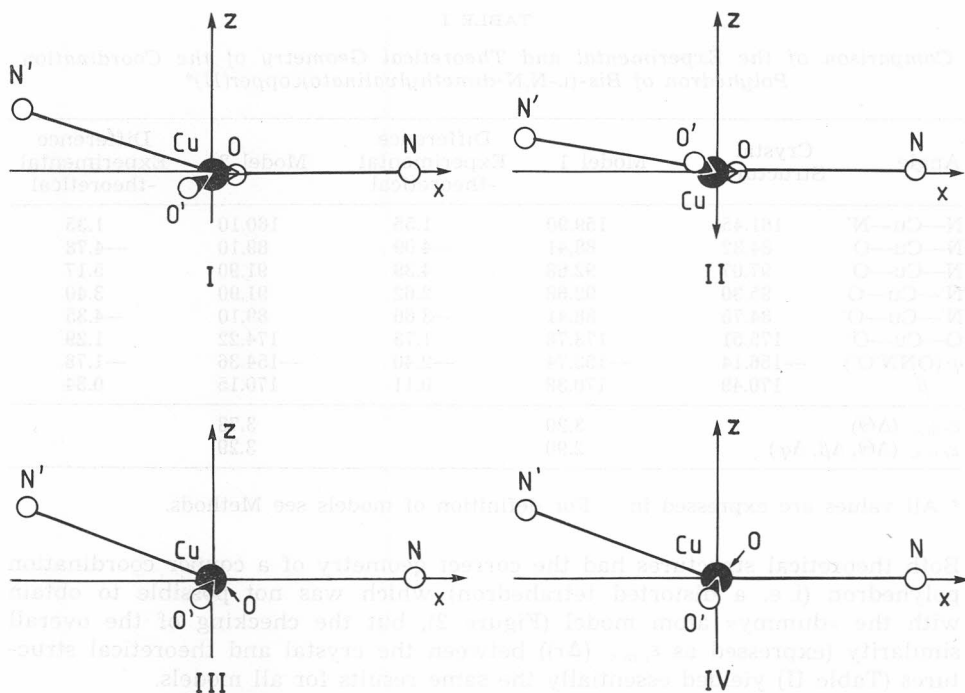


Figure 2. Shapes of copper(II) coordination polyhedron of bis-(*l*-*N,N*-dimethylvalinato)copper(II): crystal structure [I]¹⁰, »dummy« atom model FF2 [II]¹⁰, Model 1 [III] and Model 2 [IV].

with the »dummy« atom model ($\epsilon_{r.m.s.}(\Delta r) = 0.14$ Å v. s. $0.13 \dots 0.17$ Å¹⁰). It seems that our Model 1 better reproduces the overall molecular geometry than Model 2, but the differences are practically negligible. Also, new models yielded a slightly different conformation of chelate rings. In contrast to the »dummy« atom model^{9,10} which after the minimization of conformational energy yielded exactly the same conformation at both chelate rings, our new models lead to chelate rings differing from each other by 0.001 Å, in $\epsilon_{r.m.s.}(\Delta r)$ or 0.02° in r.m.s. deviations for torsional angles. These differences are at least one order of magnitude less than the differences between the ring conformations observed in the crystal structure¹⁰ ($\epsilon_{r.m.s.}(\Delta r) = 0.07$ Å error in estimation of torsional angles from 0.2 to 8°). Therefore, it stands to reason that the observed difference between chelate ring conformations in the crystal structure is caused by intermolecular interactions rather than by intramolecular ones.

The estimated diastereoselectivity (enantioselectivity) depends slightly on the procedure of calculation. It can be calculated (neglecting the vibrational contribution to Gibbs energy) from the conformational potential (Table III),

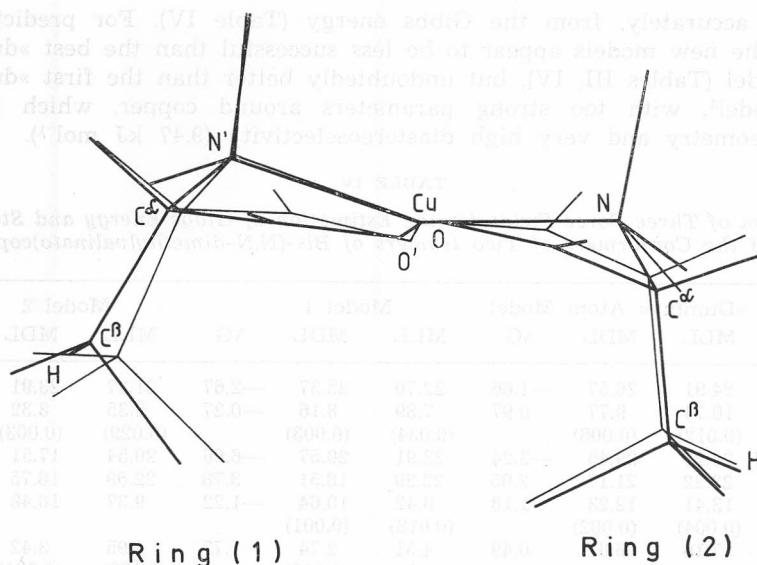


Figure 3. Comparison of the X-ray structure¹⁰ (heavy line) and the theoretical structure, Model 1 (thin line) of bis-(L-N,N-dimethylvalinato)copper(II).

TABLE III

Comparison of Three Force Fields for the Estimation of Conformational Potential and Statistical Weights of the Two Isomers of Bis-(N,N-dimethylvalinato)-copper(II)*

No.	»Dummy« Atom Model			Model 1			Model 2		
	MLL	MDL	ΔV	MLL	MDL	ΔV	MLL	MDL	ΔV
1-3	26.57	29.49	-2.92	28.49	31.63	-3.14	28.20	31.43	-3.23
1-6	11.56 (0.009)	10.56 (0.003)	0.10	11.99 (0.007)	10.74 (0.001)	1.25	11.79 (0.009)	10.46 (0.001)	1.33
3-3	27.05	33.04	-5.99	27.88	34.49	-6.61	27.65	20.32	7.33
3-4	27.22	24.86	2.36	28.44	22.84	5.60	28.39	22.67	5.72
3-6	12.88 (0.005)	11.59 (0.002)	1.29	13.28 (0.004)	11.57 (0.001)	1.71	13.12 (0.005)	11.31 (0.001)	1.81
4-6	9.50 (0.021)	10.20 (0.004)	-0.70	7.20 (0.051)	7.31 (0.005)	-0.11	7.06 (0.054)	7.21 (0.005)	-0.15
5-5	29.28	28.22	1.06	29.86	25.43	4.43	30.05	25.67	4.38
6-6	0.00 (0.062)	-3.48 (0.989)	3.48	0.00 (0.933)	-5.98 (0.992)	5.98	0.00 (0.930)	-6.01 (0.993)	6.01

Estimated diastereoselectivity 3.73 6.43 6.50
Experimental value¹³ 2.9... 4.0

* All energy values are expressed in kJ mol^{-1} . Statistical weights are given in parentheses. The »dummy« atom model corresponds to force field FF2, ref. 10. Minima of conformational energy are denoted as in ref. 5. Parameters: $k_3 = 37.5 \text{ kcal mol}^{-1} \text{ rad}^{-2}$, $\beta_0 = 180^\circ$; Model 1 $k_{\text{NMO}} = 250 \text{ kcal mol}^{-1} \text{ rad}^{-2}$; Model 2 $k_z = 500 \text{ kcal mol}^{-1}$, $h = 0$ (eq. 7). Zero points: $26.92 \text{ kJ mol}^{-1}$ for »dummy« atom model, $32.91 \text{ kJ mol}^{-1}$ for Model 1, and $34.40 \text{ kJ mol}^{-1}$ for Model 2. For definition of Model 1 and Model 2 see Methods. Diastereoselectivity was calculated from energy of all 21 conformers.

or more accurately, from the Gibbs energy (Table IV). For prediction of energy, the new models appear to be less successful than the best »dummy« atom model (Tables III, IV), but undoubtedly better than the first »dummy« atom model⁵, with too strong parameters around copper, which yielded planar geometry and very high diastereoselectivity (9.47 kJ mol⁻¹).

TABLE IV

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

No.	»Dummy« Atom Model			Model 1			Model 2			
	MLL	MDL	ΔG	MLL	MDL	ΔG	MLL	MDL	ΔG	
1—3	24.91	26.57	-1.66	22.70	25.37	-2.67	21.27	23.91	-2.64	
1—6	10.74 (0.012)	9.77 (0.006)	0.97	7.89 (0.034)	8.16 (0.003)	-0.27	8.35 (0.029)	8.32 (0.003)	0.03	
3—3	26.21	29.45	-3.24	22.91	29.57	-6.66	20.54	17.51	3.03	
3—4	23.22	21.17	2.05	22.29	18.51	3.78	22.09	16.75	5.34	
3—6	13.41 (0.004)	12.23 (0.002)	1.18	9.42 (0.018)	10.64 (0.001)	-1.22	9.37	10.48	-1.11	
4—6	7.16 (0.052)	6.67 (0.022)	0.49	4.51 (0.131)	2.74 (0.022)	1.77	4.95 (0.133)	3.42 (0.024)	1.53	
5—5	29.24	26.61	2.63	29.87	23.42	6.45	30.98	22.96	8.02	
6—6	0.00 (0.929)	-2.70 (0.967)	2.70	0.00 (0.810)	-6.60 (0.971)	6.60	0.00 (0.830)	-5.79 (0.968)	5.79	
Estimated diastereoselectivity			2.95				7.43	6.56		
Experimental value ¹³							2.9... 4.0			

* See footnote to Table III. T = 298.16 K. Zero points: 1061.91 kJ mol⁻¹ for »dummy« atom model, 1097.19 kJ mol⁻¹ for Model 1, and 1100.89 kJ mol⁻¹ for Model 2.

The fact that virtually the same results were obtained by models differing in the analytical form of potential V_{NMO} can be accounted for by the shape of coordination polyhedron in the crystal structure which is more planar than tetrahedral (the maximum value of NMO angle is 97.1°), i.e. all the final values of NMO angles are placed on the same »side« of the two-well potential curve. The only conformer which has the NMO angle values closer to tetrahedral geometry, denoted as 3-3LD (Table II), has such high energy that its influence on the overall stability of the complex is negligible.

In conclusion we can state that the newly proposed models with the distortion potential proved to be capable of reproducing fairly well the geometry and energy of bis-(N,N-dimethylvalinato)copper(II). Our future research should show whether they are applicable to other distorted structures.

REFERENCES

1. J. Gažo, I. B. Bersuker, J. Garaj, M. Kobašova, J. Kohout, H. Langfelderova, M. Melnik, M. Serátor, and F. Valach, *Coord. Chem. Rev.* **19** (1976) 253.
2. B. J. Hathaway, *ibid.* **41** (1982) 423.
3. J. Gažo, *Pure Appl. Chem.* **38** (1974) 279.

4. J. H. Ritsma, G. A. Wieggers, and F. Jellinek, *Rec. Trav. Chim. Pays-Bas*, **84** (1965) 1577.
5. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **56** (1983) 79.
6. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **57** (1984) 1217.
7. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **58** (1985) 127.
8. S. R. Niketić, Kj. Rasmussen, F. Woldbye, and S. Lifson, *Acta Chem. Scand.* **A30** (1976) 485.
9. N. Raos, S. R. Niketić, and Vl. Simeon, *J. Inorg. Biochem.* **16** (1982) 1.
10. B. Kaitner, B. Kamenar, N. Paulić, N. Raos, and Vl. Simeon, *J. Coord. Chem.* **15** (1987) 373.
11. S. R. Niketić and Kj. Rasmussen, *The Consistent Force Field: A Documentation*, Springer-Verlag, Berlin 1977.
12. Kj. Rasmussen, *Potential Energy Functions in Conformational Analysis*, Springer-Verlag, Berlin 1985.
13. V. A. Davankov, S. V. Rogozhin, A. A. Kurganov, and L. Ya. Zhuchkova, *J. Inorg. Nucl. Chem.* **37** (1975) 369.

SAŽETAK

Simulacija plastičnosti koordinacijskog poliedra bakra(II): model empirijskog polja sila s potencijalom ovisnim o distorzijskoj koordinati

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Da bi se reproducirala geometrija tetrakoordiniranih kelata dvovalentnog bakra s »distordiranim« koordinacijskim poliedrom (prelazni oblici između tetraedra i planarne konfiguracije) uvedene su dvije nove empirijske funkcije za proračun konformacijskog potencijala. Prva funkcija ovisi o distorzijskoj koordinati β , definiranoj kao kut između polovišta dvaju valencijskih kuteva oko centralnog atoma. Druga funkcija je potencijal promjene valencijskog kuta s dva minimuma (pri 90 i 109,47°) za kuteve oko bakra.

Nove funkcije iskušane su na molekuli bis-(*N,N*-dimetilvalinato)bakra(II). Metodom usklađenog polja sila (consistent force field, CFF) računski je polučena ispravna geometrija bakrove koordinacije, tj. distordirani tetraedar. Valencijski kutevi oko bakra (N—Cu—N, O—Cu—N i O—Cu—O) vrlo su dobro reproducirani, dajući korijen razlika srednjih kvadrata odstupanja od kristalne strukture u iznosu od 3,20° (model s kvadratnom funkcijom za potencijal promjene valencijskih kuteva) i 3,73° (potencijal s dva minimuma). Izmjerena diastereoselektivnost [razlika Gibbsove energije između Cu(L-ligand)₂ i Cu(L-ligand)(D-ligand)] reproducirana je unutar 3 kJ mol⁻¹.