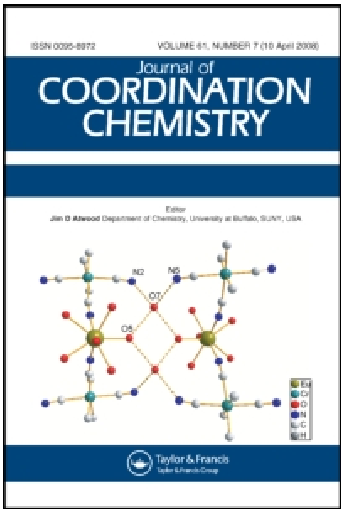

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. IV. CRYSTAL STRUCTURE OF DISORDERED *D,L-BIS(N,N-DIETHYL-*α-ALANINATO)COPPER(II); MOLECULAR MECHANICS CALCULATIONS AND CONFORMATIONAL ANALYSIS OF COPPER(II) *N,N*-DIETHYLALANINATES

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The crystal structure of a new, red, triclinic modification of (*D,L-N,N*-diethyl-α-alaninato)copper(II) was solved by X-ray diffraction methods and refined to $R = 0.035$. The structure contains discrete molecules disordered over two sites in a 72:28 ratio with the copper atom on an inversion centre. The copper, oxygen and nitrogen atoms and one carbon atom are common to both molecules while six carbon atoms are disordered over two sites. The coordination around the copper atom is irregular square-planar with oxygen and nitrogen atoms necessarily *trans*. Interatomic distances [Cu–O 1.910(2) Å and Cu–N 2.033(2) Å] are comparable with those found in related crystal structures. The two independent molecules *A* and *B* (which are disordered about an inversion centre) have identical conformations in the lattice. molecular mechanics calculations correctly predict the crystal (most stable) conformation of *D,L-bis*(*N,N*-diethyl-α-alaninato)copper(II); the conformation predicted for the *L,L* isomer appears to be a transition state between two conformations of high energy.

Keywords: Copper, *L-bis*(*N,N*-diethyl-α-alaninato)copper(II), *D,L-bis*(*N,N*-diethyl-α-alaninato)copper(II), X-ray crystal structure, conformation, molecular mechanics

INTRODUCTION

Copper(II) chelates with *N*-alkylated α-amino acids are interesting both stereochemically and biochemically. These complexes can be regarded as model compounds for the study of interactions of heavy metals with amino acids and peptides. From the stereochemical point of view they have been investigated because of pronounced diastereoselectivity effects[1,2]‡ (which has been used for chromatographic separations of racemic mixtures of amino acids[3]) and also because of steric effects leading to

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‡ Defined as $\Delta G = -RT \ln(\beta_{MLL}/\beta_{MDL})$, where β is stability constant for the corresponding diastereomer (usually enantiomer).

distortion of the copper(II) coordination polyhedron.[4] The task of reproducing the shape of the coordination polyhedron (intermediate in structure between planar and tetrahedral) in these complexes by means of molecular mechanics method led us to propose three kinds of theoretical models, namely the "dummy" atom model,[5] a model with the potential dependent on distortion coordinate[6,7] and an electrostatic model.[8] The last two models were well able to reproduce the shape of the copper(II) coordination polyhedron.

In an attempt to study the *D,L* and *L,L* isomers of *bis*(*N*,*N*-diethylalaninato)-copper(II) and compare it with the known *D,L* isomer[9], we prepared quite accidentally what we now know to be a disordered form of the known *D,L* isomer. This paper compares the disordered *D,L* structure with the previously published ordered one[9] and discusses the observed crystal structure in the terms of observed conformations predicted from molecular mechanics calculations.

EXPERIMENTAL

The ligand *L*-*N*,*N*-diethylalanine (yield 40%, M.p. 120°C) was synthesized in the same way as the racemic ligand,[9] *i.e.*, by condensation of the amino acid with acetaldehyde, followed by hydrogenation.[16] The Cu-complex was prepared by reaction of the ligand and copper(II) acetate monohydrate in dry benzene (dried over sodium). After slow evaporation of the solvent from the benzene/ethanol solution red and blue crystals appeared.

Our intention had been to prepare the blue **aqua** *L,L* and a red **non-aqua** *L,L* complexes. We have already described the structure of the blue *L,L* complex[15] and report here the analysis of the red crystals, which to our surprise turned out to be a disordered form of the *D,L* complex, and presumably arise from impurities or racemization of the starting material.

Crystal structure determination

Crystal data:

$C_{14}H_{28}CuN_2O_4$, $M_r = 351.93$, triclinic, space group $P\bar{1}$, $a = 7.454(3)$, $b = 8.092(3)$, $c = 8.210(2)$ Å, $\alpha = 118.69(4)$, $\beta = 93.78(3)$, $\gamma = 100.46(3)°$, $V = 420.5(3)$ Å^3, $Z = 1$, $D_x = 1.390\,\mathrm{g\,cm^{-3}}$, $F(000) = 187$, $\lambda(\mathrm{Mo}\,K\alpha) = 0.7093$ Å, $\mu(\mathrm{Mo}\,K\alpha) = 13.2\,\mathrm{cm^{-1}}$.

X-ray measurements on a crystal of dimensions $0.35 \times 0.17 \times 0.17$ mm were made at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were determined from the setting angles of 25 reflections ($17 < 2\theta < 33°$). Intensity data were measured with ω-2θ scans in the 2θ range 4 to 54°, reflection indices range $h -9 \rightarrow 9$, $k\, 0 \rightarrow 10$, $l -10 \rightarrow 10$. Three standard reflections measured every one hour showed no significant variation over the period of data collected. A total of 1836 reflections were measured, of which 1688 were considered observed [$I \geqslant 3\sigma(I)$] and were used in structure analysis. Lorentz and polarization corrections were applied to the intensity data. Gaussian numerical correction for absorption was performed (the minimum and maximum transmission factors were 0.798 and 0.841, respectively).

Our first attempt to solve the structure was based on the assumption that we were determining the crystal structure of an *L,L*-isomer. The standard heavy-atom method was used. The coordinates of the copper atom were chosen as 0,0,0 to determine the origin of the space group $P1$. The position of all non-hydrogen atoms were found from the subsequent difference Fourier syntheses. Isotropic followed by anisotropic refinement procedure of the non-H atoms followed by generating the hydrogen atoms in their geometrically expected position gave us quite inadequate results. Although the R factors were fairly low ($R = 0.047$, $R_w = 0.052$) some bond distances, bond angles and the anisotropic thermal parameters were nonsensical. Analysis of the E statistics indicated that the structure was centrosymmetric and not acentric, but if the structure were centrosymmetric we would have a *D,L* system and not *L,L* as we had anticipated. The *D,L* structure has already been described by Nash and Schaefer[9] (henceforth NS). NS reported their *D,L* structure in a non-reduced cell, which when reduced gives essentially the same cell (the NS reduced cell has $a = 7.495$, $b = 8.101$, $c = 8.163$ Å, $\alpha = 118.69$, $\beta = 94.16$, $\gamma = 100.57°$) as we report above. Accordingly we took the positional parameters from NS, transformed them into the reduced cell setting, and carried out a refinement with our reflection data. This led to R being 0.073, and a difference synthesis clearly revealed the presence of unanticipated peaks in our maps. We had previously taken NS's coordinates and data and refined their structure with the NRCVAX[18] programs, and have confirmed the correctness of their work in that it led to featureless difference maps.

Careful inspection of electron density and difference Fourier maps calculated with our data led us to the conclusion that asymmetric carbon atom C2 was disordered unequally over two sites, with corresponding disorder of the ethyl substituents on the nitrogen atom. From electron density peak heights we initially assumed a 0.70/0.30 ratio of the carbon atoms and careful inspection of the models that this produced showed that the two models had essentially the same conformation, B being simply related to A by a 180° rotation about a line normal to the CuO_2N_2 coordination plane so that the atoms Cu, O1, O2, N and C1 occupied identical sites in the two models. Because of the relatively low occupancy of the B molecule we opted for the constrained refinement of this model using the constraints in *SHELX76*[19] with the B molecule C–C and C–N bond lengths constrained to be within 0.01 Å of those for the much more reliable A model. We also refine the relative A/B occupancy factor. The non-hydrogen atoms were allowed anisotropic thermal parameters. At the positions anticipated for the hydrogen atoms small diffuse positive electron densities were found. The hydrogen atoms were placed in calculated positions riding on their bonded carbon atoms. The variable parameters were refined using full-matrix least-squares methods with a weighting scheme $w = 1/[\sigma^2(F_0) + 0.00251(F_0^2)]$. Final $R = 0.035$, $R_w = 0.038$, and $S = 0.909$ for 154 variables. The largest Δ/σ was 0.16 for the final cycle of refinement and the range of electron densities in the final difference Fourier map was from $+0.60$ to $-0.36\,e\text{Å}^{-3}$. The occupancy factor refined to 0.72/0.28. The atomic scattering factors for the neutral atoms and anomalous dispersion coefficients were taken from the *International Tables for X-ray Crystallography.*[17] Computations were carried out with *NRCVAX*[18] on a Silicon graphics 4D-380 computer and *SHELX76*[19] on an IBM3081K computer.

Final fractional atomic coordinates are listed in Table I and selected interatomic parameters are given in table II. Full lists of bond distances, bond and torsion angles, calculated hydrogen atoms coordinates, anisotropic thermal parameters and observed and calculated structure factor tables are available from the Editor on request.

TABLE I
Atomic coordinates of non-hydrogen atoms $(\times 10^4)$ and equivalent isotropic thermal displacement coefficients B_{eq}(Å^2).

	x/a	*y/b*	*z/c*	B_{eq}*	*occ.*
Cu	5000	5000	5000	2.77(1)	
O1	6606(3)	3272(3)	4338(3)	4.80(7)	
O2	6644(3)	166(3)	2936(4)	5.59(8)	
N	2974(3)	2529(3)	3381(3)	3.56(7)	
C1	5832(4)	1460(4)	3457(4)	3.99(9)	
C2A	3807(5)	994(5)	3476(6)	4.0(1)	0.72
C3A	2802(9)	−1096(7)	2014(11)	6.1(2)	0.72
C4A	1165(5)	2536(6)	3881(6)	4.3(1)	0.72
C5A	1141(8)	2998(10)	5938(9)	5.1(2)	0.72
C6A	2931(6)	2130(6)	1352(5)	4.6(1)	0.72
C7A	2799(11)	3842(15)	1141(12)	6.5(3)	0.72
C2B	3897(10)	1063(9)	2230(10)	3.5(3)	0.28
C3B	2898(16)	−1065(11)	1292(21)	7.0(7)	0.28
C4B	2080(13)	1986(15)	4797(14)	4.7(4)	0.28
C5B	1770(33)	3690(25)	6477(22)	9.1(1.4)	0.28
C6B	1328(11)	2853(14)	2507(14)	4.4(3)	0.28
C7B	1945(21)	3513(35)	1095(27)	6.0(7)	0.28

* B_{eq} is the mean of the principal axes of the thermal ellipsoid.

TABLE II
Bond distances (Å), bond angles and selected torsion angles(°).

	Crystal structure molecule *A*	Theoretical structure (M6)
Bond distances		
Cu–O1	1.910(2)	2.001
Cu–N	2.033(2)	2.052
O1–C1	1.275(3)	1.282
O2–C1	1.217(3)	1.241
N–C2A	1.517(4)	1.487
N–C4A	1.435(4)	1.490
N–C6A	1.533(4)	1.489
C1–C2A	1.491(4)	1.521
C2A–C3A	1.528(6)	1.551
C4A–C5A	1.547(7)	1.549
C6A–C7A	1.496(9)	1.548
Bond angles		
O1–Cu–N	84.1(1)	83.51
O1′–Cu–N	95.9(1)	96.49
Cu–O1–C1	116.7(2)	113.2
Cu–N–C2A	102.6(2)	101.9
Cu–N–C4A	116.7(2)	111.4

TABLE II
Continued.

	Crystal structure molecule *A*	Theoretical structure (M6)
Cu-N-C6A	105.5(2)	107.4
C2A-N-C4A	113.9(3)	113.2
C2A-N-C6A	105.8(3)	111.2
C4A-N-C6A	111.3(3)	111.2
O1-C1-O2	125.2(3)	121.5
O1-C1-C2A	114.2(2)	114.2
O2-C1-C2A	119.2(3)	124.2
N-C2A-C1	109.0(3)	108.8
N-C2A-C3A	114.6(4)	113.5
C1-C2A-C3A	113.6(4)	111.8
N-C4A-C5A	113.5(3)	113.3
N-C6A-C7A	113.5(5)	112.6
Torsion angles		
O1-Cu-N-C4A	150.4(3)	150.0
Cu-O1-C1-O2	−179.8(3)	164.4
Cu-N-C2A-C1	−37.5(3)	−43.8
C4A-N-C2A-C1	−164.6(3)	−163.5
C6A-N-C2A-C1	72.9(4)	70.4
Cu-N-C4A-C5A	−56.9(5)	−58.0
C6A-N-C4A-C5A	−178.2(4)	−177.9
C2A-N-C6A-C7A	−159.5(5)	−160.9
O1-C1-C2A-N	35.6(4)	42.2
O2-C1-C2A-N	−157.1(3)	−137.9
N-Cu-O1-C1	−8.0(2)	−8.5
Cu-O1-C1-C2A	−13.4(4)	−15.7
Cu-N-C2A-C3A	−166.0(4)	−169.0
C4A-N-C2A-C3A	66.9(5)	71.3
C6A-N-C2A-C3A	−55.7(5)	−54.8
C2A-N-C4A-C5A	62.4(5)	56.1
Cu-N-C6A-C7A	−51.3(6)	−50.3
C4A-N-C6A-C7A	76.3(6)	71.9
O1-C1-C2A-C3A	164.7(4)	168.4
O2-C1-C2A-C3A	−28.1(6)	−11.7

Symmetry code ('): $-x+1,\ -y+1,\ -z+1$.

Conformational analysis

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

$$V = 1/2\sum_i k_{b,i}(b_i - b_{o,i})^2 + 1/2\sum_j k_{\theta,j}(\theta_i - \theta_{o,j})^2 + 1/2\sum_k V_n(1 \pm \cos n\varphi_k) + \sum_l [\mathrm{A}_l \exp(-\mathrm{B}_l \mathrm{r}_l) - \mathrm{C}_l \mathrm{r}_l^{-6}] + 1/2\sum_m \mathrm{k}_{\chi,m}\chi_m^2 + 1/2\mathrm{k}_\beta(\beta - \beta_o)^2 + \mathrm{V}_{XMY} + V_{el} \qquad (1)$$

where b, θ, φ and χ stand for bond lengths, valence, torsion and out-of-plane angles, respectively, r is the non-bonded distance and β is a distortion coordinate defined as an angle between the bisectors of two opposite (N–Cu–O and N′–Cu–O′) valence angles around copper. K_b is an empirical parameter for bond stretching and k_θ for valence angle bending. Torsion interactions were determined with parameters V_n and n (height and multiplicity of the torsion 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 groups with a quadratic function dependent on the parameter k_χ was also computed.

The last three terms in equation (*1*) were determined by an appropriate model for distortion of the coordination polyhedron. We have proposed altogether three kinds of model: a "dummy" atom model[5] (FF1–FF3a), a model with a distortion coordinate[6,7] (M3–M5), and an electrostatic model[8] (M6). The quadratic potential dependent on the distortion coordinate and parameters k_β and β_o is specific for force fields M3–M5.[7] The potential V_{XMY} is an angle-bending potential for the angles around copper, which can be quadratic (FF1–FF3a, M3) or in the form of a two well parabola expressed by a cosine power series (M4, M5). V_{el} is a coulombic potential between four ligand atoms and two point charges situated above and below the plane of the chelate rings (M6).[8] The potential dependent on the atoms around copper, when using the "dummy" atom model (FF1–FF3a), is determined only by the quadratic angle bending interactions between four "real" and two "dummy", apically placed atoms. A short overlay of models and parameters was given in our previous paper.[14] Calculations were performed with a program developed by Kj. Rasmussen and co-workers[20] which have been modified to cope with the new empirical potentials.

The root-mean-square deviation between crystal and theoretical structures was calculated from (2),

$$\varepsilon_{\mathrm{r.m.s.}}(\Delta r)=\left[(1/N)\sum_{i=1}^{N}(\Delta r_i)^2\right]^{1/2} \tag{2}$$

where r stands for interatomic distance (only non-hydrogen atoms were taken into account). Δ denotes the difference between the values of r in two structures.

RESULTS AND DISCUSSION

Description of the crystal structure

The general view of the complex (Figure 1) shows two centrosymmetric molecules *A* and *B*. Our analysis shows that the unit cell contains one molecule of the *D*,*L*-complex which is disordered 72/28 in such a way that the Cu, O1, O2, N and C1 atoms are common to both molecules. The remaining carbon atoms are disordered over two sites in a 72/28 ratio. The two isomers *A* and *B* have identical conformation (*B* is simply related to *A* by a 180° rotation about a line normal to the CuO_2N_2 coordination plane) and are in perfect agreement with the conformer reported by NS. The Cu–O1 1.910(2) and Cu–N 2.033(2) Å bond lengths and O–Cu–N 84.1(1)° and O′–Cu–N 95.9(1)° bond angles are comparable with those found in related structures, *e.g.*, in *bis*(*L*-*N*,*N*-dimethylvalinato)copper(II)[13] the corresponding averaged values are 1.899(2) Å, 2.024(3) Å, 84.4(1)° and 96.3(1)°, and in *bis*(*L*-*N*,*N*-dimethylisoleucinato)copper(II)[14] are 1.899(5) Å, 2.008(4) Å, 84.3(2)° and 96.0(2)°. The bond

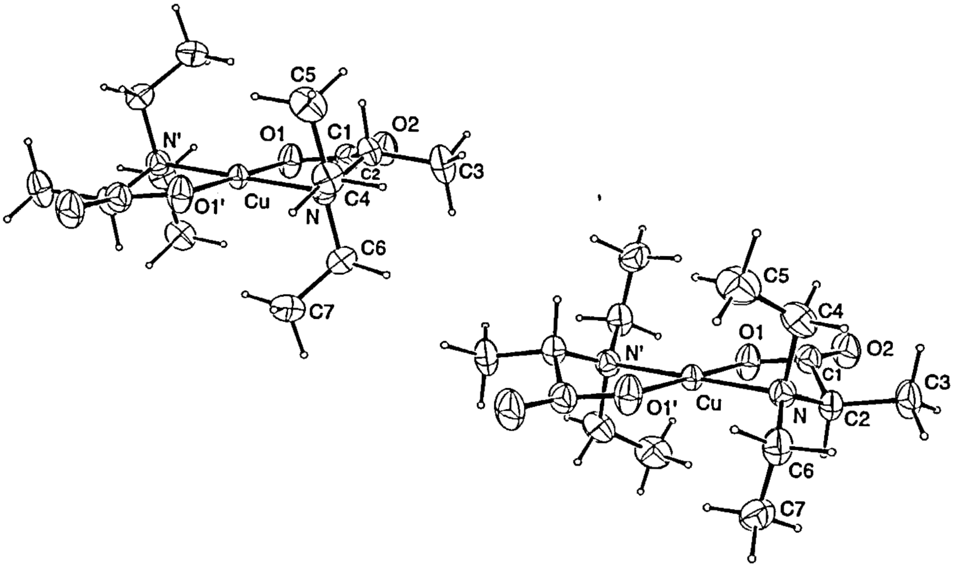


FIGURE 1 An *ORTEP*II (Johnson, 1976) view of molecule *A* (top) and molecule *B* (bottom) showing atom labelling scheme. The two molecules lie on the same inversion centre and have the non-disordered Cu, O1, O2, N and Cl atoms in common. The thermal ellipsoids enclose 35% probability. Symmetry code: (')$-x+1$, $-y+1$, $-z+1$. In both molecules the five-membered chelate ring has an envelope conformation with C2 at the flap.

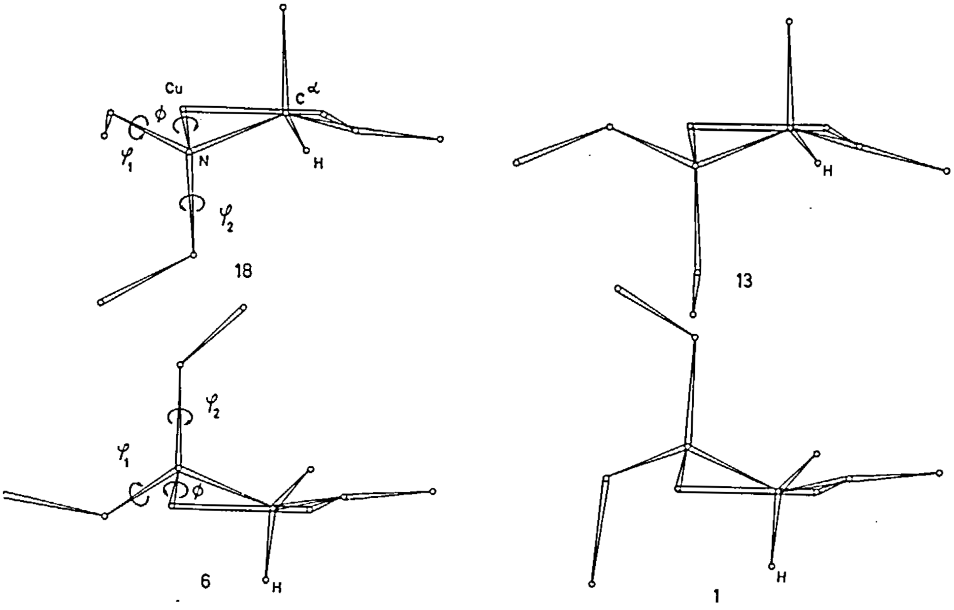


FIGURE 2 Four chelate ring conformations of *bis*(*N*,*N*-diethylalaninato)copper(II) with lowest energy (*c.f.* Table III). Torsion angle Φ corresponds to O1–Cu–N–C4, φ_1 to Cu–N–C4–C5 and φ_2 to Cu–N–C6–C7 in the crystallographic numbering scheme (Figure 1).

TABLE III
Minima of conformation energy for chelate rings of *bis*(*L*-*N*,*N*-diethylalaninato)copper(II).*

No.	Torsion angle (°) Φ	φ_1	φ_2	Strain energy (kJ mol^{-1})
1	149.53	−61.03	−54.29	1.79
2	144.22	−54.54	55.77	4.36
3	149.28	−53.61	−159.54	10.53
4	145.46	60.04	−31.95	8.15
5	146.01	24.85	−58.79	7.70
6	140.72	58.21	56.82	1.33
7	145.45	55.45	−161.55	7.41
8	139.91	179.90	−58.40	4.89
9	138.58	−176.61	52.08	4.44
10	143.44	−161.56	−160.22	20.68
11	−142.37	−64.98	−62.95	4.43
12	−148.11	−66.17	27.80	10.60
13	−148.36	−64.73	175.52	1.62
14	−146.24	28.02	−59.73	17.59
15	−151.34	18.72	50.93	13.10
16	−152.56	26.00	−178.93	13.15
17	−145.08	−179.17	−53.55	3.11
18	−149.00	−179.69	62.30	0.00
19	−150.78	178.91	−153.49	13.12

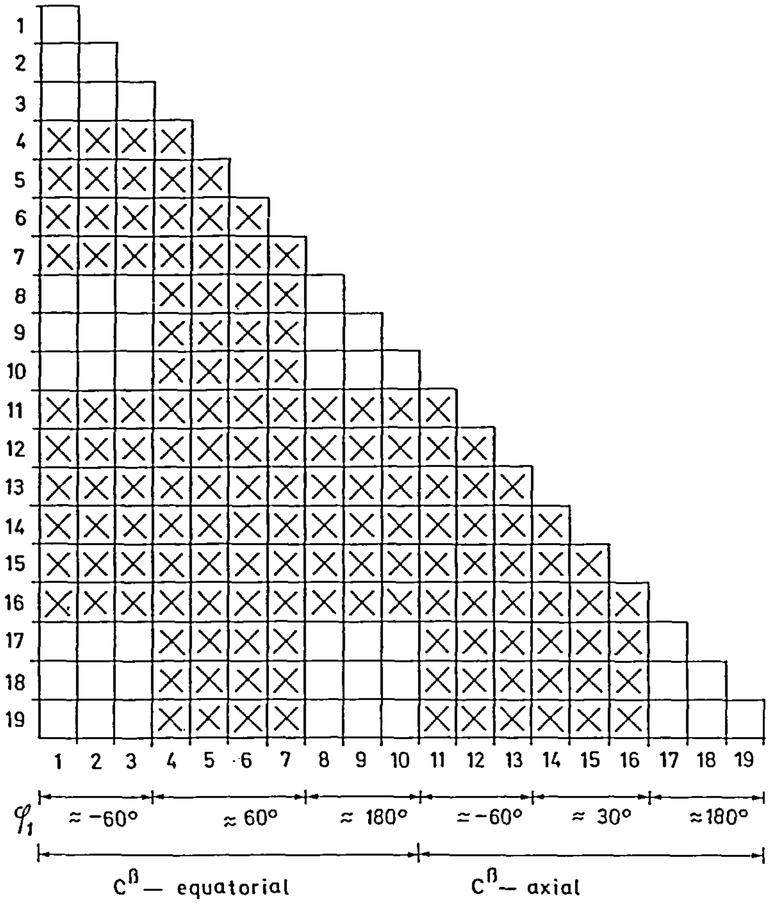
* For definition of angles see Figure 2. Calculations were performed with FF1 (see Experimental); energies are expressed relative to the lowest minimum; V(18) = 20.701 kJ mol^{-1}.

distances and angles corresponding to the *A* molecule are all within 3 e.s.d.'s of those reported by Nash and Schaefer.[9] There are no intermolecular contacts less than sum of the van der Waals radii.

Conformational analysis

By systematic change of torsion angles φ_1 and φ_2 (Figure 2), followed by minimisation of conformational potential energy, 19 stable conformations of the chelate rings were obtained (Table III) for both C^{β}-axial ($\Phi \approx -140°$) and C^{β}-equatorial ($\Phi \approx 140°$) conformations. The ring conformation observed in the crystal structure of the *D*,*L*-isomer[9] (1 in our notation) is not the lowest energy one ("global minimum"); there are three other ring conformations with lower energy (Figure 2, Table III). Two of the four lowest conformers (13 and 18) have C^{β}-axial conformation. Therefore, neither of the ring conformations (C^{β}-axial and C^{β}-equatorial) is energetically preferable.

As a molecule of the *bis* complex contains two chelate rings, there are theoretically $19(19+1)/2 = 190$ possible conformations of both *L*,*L*- and *D*,*L*-isomers of *bis*(*N*,*N*-diethylalaninato)copper(II). In order to reduce that huge number of conformers, we have constructed all the possible conformations assuming that they had the same



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1																			
2																			
3																			
4	X	X	X	X															
5	X	X	X	X	X														
6	X	X	X	X	X	X													
7	X	X	X	X	X	X	X												
8				X	X	X	X												
9				X	X	X	X												
10				X	X	X	X												
11	X	X	X	X	X	X	X	X	X	X	X								
12	X	X	X	X	X	X	X	X	X	X	X	X							
13	X	X	X	X	X	X	X	X	X	X	X	X	X						
14	X	X	X	X	X	X	X	X	X	X	X	X	X	X					
15	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X				
16	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
17				X	X	X	X				X	X	X	X	X	X			
18				X	X	X	X				X	X	X	X	X	X			
19				X	X	X	X				X	X	X	X	X	X			

FIGURE 3 Diagram of non-bonded interactions between two chelate rings of appropriate conformation (denoted as in Table III). Conformers with interaction (non-bonded) energy greater than 100 kJ mol^{-1} are marked by an X. The diagram is valid for both (*L,L* and *D,L*) isomers.

geometry for the chelate rings as in the mono complex and strictly planar coordination (Figure 3). Taking an arbitrary criterion that a conformation is "forbidden" if steric strain among the chelate rings is greater than 100 kJ mol^{-1}, 45 low-energy conformers of each isomer can be proposed. The conformers with C^β-equatorial ring conformations seem to be slightly preferred. Among the "possible" conformers there are 21 with the equatorial-equatorial, seven with the quatorial-axial and 18 with the axial-axial conformations.

Further reduction of the number of conformers was achieved by selection of only the conformers containing chelate rings with a strain energy less than 5 kJ mol^{-1} above the global minimum (see Table III). The resulting energies of 18 conformers obtained after minimization of conformational potential by using two force fields are presented in Table IV.

TABLE IV
Minima of conformation energy for *L,L*- and *D,L*-isomers of *bis*(*N,N*-diethylalaninato)copper(II).*

	L,L-isomer		*D,L*-isomer	
Conformation	FF1	M6	FF1	M6
1 1	0.39	0.09	0.00	0.00
1 2	8.21	4.28	5.40	3.64
1 8	11.27	10.35	11.11	9.76
1 9	12.05	8.54	9.60	8.34
1 17	10.96	8.24	12.62	8.71
1 18	3.84	0.29	1.75	0.25
2 2	5.41	4.72	18.74	15.31
2 8	16.90	13.25	13.17	10.98
2 9	12.95	9.85	14.28	13.18
2 17	12.93	9.93	9.52	8.58
2 18	3.19	1.97	9.97	7.95
8 17	17.63	15.66	20.26	16.26
8 18	13.67	11.09	11.69	9.74
9 17	13.83	12.92	14.94	11.41
9 18	10.02	7.19	10.79	8.06
17 17	10.47	8.09	10.31	9.66
17 18	8.95	9.93	6.93	5.23
18 18	1.25	−0.38	4.63	2.14

*All energy values were expressed in $kJ\,mol^{-1}$ with respect to lowest conformer (1-1*D,L*); $V_0=31.127\,kJ\,mol^{-1}$ (FF1), $V_0=880.642\,kJ\,mol^{-1}$ (M6). For definition of force fields (FF1 and M6) see Experimental.

Average Gibbs energies of both isomers were computed in order to predict diastereoselectivity (enantioselectivity) effects in non-aqueous solutions. From the strain energy of the proposed lowest energy conformers of the complex presented in Table IV, the differences in energy between *L,L*- and *D,L*-isomers were computed (from the Boltzman distribution) to be 0.18 and $0.56\,kJ\,mol^{-1}$ in favour of *L,L*-isomer, with the respective force fields FF1 and M6. Introduction of vibration contribution to the Gibbs energy did not substantially change the results; calculations with FF1 yielded an enantioselectivity of $0.60\,kJ\,mol^{-1}$. It is therefore evident that the enantioselectivity effect in non-aqueous solutions should be negligible.

Upon minimisation of the conformational energy both molecules (*A* and *B*) yielded the same minimum: 1-1DL, *i.e.*, the conformer with the lowest energy (Table III). The structure of the molecule is basically equivalent to the structure of *D,L-bis*(*N,N*-diethylalaninato)copper(II) as determined previously by C. P. Nash and W. Schaefer.[9] The difference with respect to NS structure calculated for molecule *A* is $\varepsilon_{r.m.s.}(\Delta r)=0.0316\,\text{Å}$. The NS structure and our molecule *A* were equally well reproduced with our theoretical models [$\varepsilon_{r.m.s.}(\Delta r)=0.0605\,\text{Å}$ for NS structure and 0.0588 Å for molecule *A*; Model 6].

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