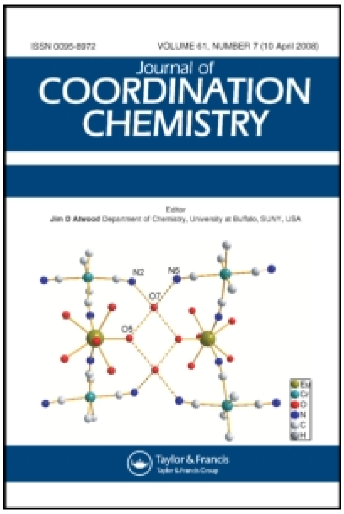

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Stereochemistry of Complexes with *N*-Alkylated Amino Acids. v. Crystal Structure, Molecular Mechanics Calculations and Conformational Analysis of Bis(*L-N,N*-Diethyl-α-Alaninato)Aquacopper(II)

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. V. CRYSTAL STRUCTURE, MOLECULAR MECHANICS CALCULATIONS AND CONFORMATIONAL ANALYSIS OF BIS(*L*-*N*,*N*-DIETHYL-α-ALANINATO)AQUACOPPER(II)

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The crystal structure of the blue, monoclinic (space group $P2_1$) modification of bis(*L*-*N*,*N*-diethyl-α-alaninato)aquacopper was solved by X-ray diffraction and refined to $R = 0.044$. Coordination around the copper(II) atom can be described as distorted square-pyramidal with nitrogen and oxygen atoms in *trans* positions (O–Cu–O 175.7°, N–Cu–N 160.0°). The Cu–O distances (1.899 and 1.945 Å) are close to values in other *N*,*N*-dialkylaminoacid complexes, but the Cu–O(w) (2.263 Å) distance is extremely short, and Cu–N (2.072 and 2.075 Å) distances are longer than usual. This is probably due to intermolecular hydrogen bonding [C=O...H–O(w)]. The conformations of chelate rings correspond to those in the structure of (*D*-*N*,*N*-diethylalaninato)(*L*-*N*,*N*-diethylalaninato)copper(II).

The shape of the coordination polyhedron was reasonably well reproduced with theoretical calculations (molecular mechanics), yielding differences between calculated and measured angles around copper of from 1.3 to 5.2°. The calculated strain energy of the crystal conformation is about 4 kJ mol^{-1} higher than the energy of the most stable conformer. This fact was tentatively attributed to the additional stabilization of molecular conformation by intermolecular hydrogen bonds.

Keywords: bis(*L*-*N*,*N*-diethyl-α-alaninato)aquacopper(II), *N*,*N*-diethyl-α-alanine, copper, X-ray structure, molecular mechanics, conformational analysis

INTRODUCTION

Our interest in copper(II) chelates with *N*-alkylated and *N*,*N*-dialkylated α-amino acids arose from two features of their chemistry. *N*-benzylproline was the first bidentate α-amino acid for which the enantioselectivity effect,† both in aqueous and non-aqueous solutions, was established[1] after many unsuccessful attempts to find enantioselectivity in systems involving naturally occurring amino acids.[2]

† Defined as $\Delta G = -RT \ln (\beta_{MLL}/\beta_{MDL})$ where β is cumulative stability constant of a corresponding bis-complex with natural (L) or enantiomeric (D) form of amino acid.

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That finding, which was later established for many other *N*-alkylated derivatives of α-amino acids,[3,4] has been extensively used for the separation of optical isomers of amino acids by means of stereoselective ligand-exchange chromatography.[5]

The second, more important reason for our research interest in *N*-alkylated copper(II) amino acidates is the fact that they can be regarded as a homologous class of tetracoordinated copper(II) complexes with distorted coordination polyhedron geometry. The distortion of tetrahalocuprates,[6–8] the most extensively studied class, cannot be investigated without taking into account packing interactions in the crystal lattice. This is not true for copper(II) chelates with *N*-alkylsalicylaldimines[9] and substituted pyrroles[10,11] which are distorted mainly because of intramolecular interactions. Unfortunately, they cannot be regarded as suitable model compounds for copper(II) chelates with naturally occurring amino acids and peptides, which are of primary interest.

These two aspects of copper stereochemistry are mutually connected. Enantioselectivity in the copper(II)/*N*,*N*-dialkylated amino acid systems could be quantitatively reproduced only if the plasticity of the copper(II) coordination polyhedron was taken into account.[9,12–15] Therefore, to treat the copper(II) complexes by molecular mechanics (or the consistent force field) method,[16,17] one must first develop an appropriate empirical model for simulation of copper(II) coordination plasticity.[18,19] We have proposed three kinds of empirical models; (1): the "dummy" atom model[20] treats tetracoordinated[9,20–22] and pentacoordinated[23,24] copper(II) complexes as if they were octacoordinated; (2): the model with distortion potential[14,25] introduces an additional internal coordinate in the copper coordination polyhedron and a potential dependent on it; (3): a model with coulombic interactions[15] assumes that the interactions in the first coordination sphere are essentially ionic. The "dummy" atom model did not prove to be very successful in reproducing the shape of the coordination polyhedron in tetracoordinated copper(II) complexes,[9,21,22] but it seems to be suitable for conformation analysis of copper(II) complexes with an apically coordinated water molecule.[24]

The aim of this paper is to discuss, by using the molecular mechanics method, the X-ray structure of pentacoordinate bis-(*L*-*N*,*N*-diethylalaninato)aquacopper(II). The crystal structure of a similar (but square-planar) complex, bis(*L*-*N*,*N*-diethylalaninato)copper(II), has been published recently[26] and therefore our principal task will be to find how additional apical ligation of the water molecule influences the strain energy of conformers. A no less important aim of our research is to check the molecular mechanics models and parameters in order to come closer to our ultimate goal of developing a method which should provide a deeper (*i.e.* quantitative) insight into the conformational properties of copper(II) chelates with flexible geometry.

EXPERIMENTAL

Crystal structure determination

$C_{14}H_{30}CuN_2O_5$, $M_r = 369.95$, monoclinic, space group $P2_1$, $a = 8.249(1)$, $b = 11.455(1)$, $c = 10.225(1)$ Å, $\beta = 113.91(1)°$, $V = 883.3(2)$ Å^3, $Z = 2$, $D_x = 1.391$ gcm^{-3}, $F(000) = 394$, λ (MoKα) = 0.7107 Å, $\mu = 12.60$ cm^{-1}.

Crystals were obtained by recrystallization from benzene/ethanol (details of the preparation are given elsewhere[26–28]). X-ray data for a prismatic blue crystal (0.30 × 0.25 × 0.25 mm) were collected at room temperature on a Philips PW1100 diffractometer using graphite-monochromatized MoKα radiation. Lattice parameters and their estimated standard deviations were derived from the setting angle of 21 reflections ($6 < \theta < 15$). The space group was determined from observed systematic absences and structure determination as $P2_1$. A total of 1665 reflections ($\theta < 27°$; $\theta/2\theta$ scan; $0.06°\,s^{-1}$; $-10 < h < 10, 0 < k < 14, 0 < l < 12$) were scanned. Three reference reflections showed no decay during the X-ray exposure time. The intensities were corrected for Lorentz and polarization effects but not for absorption and merged into a set of 1576 unique reflections ($R_{int} = 0.029$). The 1482 reflections with $F_o > 2\,\sigma(F_o)$ were used in the subsequent structure analysis. The structure was solved by means of the heavy-atom method. Refinement was carried out by full-matrix least-square techniques on F's. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms could be located as low positive maxima in a difference Fourier map and were included in structure factor calculations in their expected geometric positions, but they were not refined. The isotropic thermal parameters were refined separately for hydrogen atoms in the water molecule, hydrogen atoms in the CH and CH_2 groups, and hydrogens in CH_3 groups. Convergence was reached at $R = 0.044$, $R_w = 0.043$, $w = 0.792(\sigma^2(F_o) + 0.0005(F_o)^2)$, $S = 0.88$, $(\Delta/\sigma)_{max} = 0.004$, $\Delta\rho_{min} = -0.37, \Delta\rho_{max} = 0.44\,e\text{Å}^{-3}$. Atomic coordinates and equivalent isotropic thermal parameters are given in Table I. Scattering and anomalous dispersion factors were taken from International Tables for X-ray Crystallography.[29] Refinement, geometric calculations and plotting was performed with the set of crystallographic programmes CRYSRULER PACKAGE I[30] (Shelx-76, Multan-80, Pluto-78, Ortep-II and Parst). All calculations were carried out on an IBM PC/AT compatible microcomputer (80386/25 MHz microprocessor and mathematical 80387 coprocessor).

TABLE I

Final fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters U_{eq} ($\times 10^3$; $\times 10^4$ Å^2 for Cu) with e.s.d.'s in parentheses; $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Atom	x/a	y/b	z/c	U_{eq}
CU	2270(1)	0	−1(1)	248(2)
O	−476(6)	3(8)	−7(6)	65(2)
O11	2328(9)	1656(8)	−49(6)	46(3)
O12	2755(7)	3227(5)	1337(7)	57(3)
O21	2388(9)	−1696(8)	53(7)	52(4)
O22	1434(8)	−3248(5)	−1336(7)	61(3)
N1	3795(7)	227(7)	2164(7)	44(3)
N2	1618(8)	−227(6)	−2169(6)	43(3)
C11	2744(9)	2171(7)	1143(9)	44(3)
C12	3113(10)	1366(7)	2439(8)	46(3)
C13	4214(12)	1949(9)	3872(9)	64(4)
C14	3772(12)	−724(9)	3162(10)	63(4)
C15	1994(14)	−873(9)	3226(12)	78(5)
C16	5696(10)	378(7)	2347(10)	57(3)
C17	6467(13)	−698(9)	1910(12)	76(5)
C21	1579(9)	−2176(7)	−1179(9)	41(3)
C22	696(10)	−1378(7)	−2448(8)	45(3)
C23	352(12)	−1982(9)	−3868(9)	64(4)
C24	601(11)	685(8)	−3169(8)	52(4)
C25	−1249(11)	868(10)	−3242(12)	80(4)
C26	3363(12)	−394(8)	−2336(11)	60(4)
C27	4561(12)	674(9)	−1904(12)	73(5)

Conformational analysis

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

$$V = 1/2 \sum_{i} k_{b,i}(b_i-b_{o,i})^2 + 1/2 \sum_{j} k_{\theta,j}(\theta_j-\theta_{o,j})^2 + 1/2 \sum_{k} V_n(1 \pm \cos n\varphi_k) + \sum_{l}(A_l \exp(-B_l r_l)-C_l r_l^{-6}) + 1/2 \sum_{m} k_{\chi,m}\chi_m^2 + 1/2\, k_\beta(\beta-\beta_o)^2 + V_{cis} + V_{trans} + V_{el} \qquad (1)$$

where b, θ, φ, and χ stand for bond lengths, valence, torsional and out-of-plane angles, respectively, r is a 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. 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 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 [the "dummy" atom model[20] (FF1–FF3a), the model with a distortion coordinate[14,25] (M3–M5) and the electrostatic model[15] (M6)]. The quadratic potential dependent on distortion coordinate β and parameters k_β and β_o is specific for force fields M3–M5. The potential V_{cis} is angle-bending potential for the cis (N–Cu–O) 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_{trans} is an additional angle-bending potential for *trans* angles in the form of a two-well parabola (M5). V_{el} is the coulombic potential between four ligand atoms and two point charges situated above and below the plane of the chelate rings (M6). 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.

The force fields based on the "dummy" atom model can be grouped into "weak" (FF2–FF3a) and "strong" (FF1) ones because of large differences in values of k_{N-Cu-O} parameters. Also, they can be described as symmetrical force fields (FF1, FF3, FF3a), with equal parameters for all *cis* angles and asymmetrical ones (FF2, FF2a), with the subsequently weaker k_θ parameters for the apically situated ligand. The force fields denoted with a prime (*e.g.* FF2′) have an additional non-bonding potential (the same parameters as for the oxygen atom) with the apically situated atom. A short overlay of models and parameters was given in a previous paper.[22] Calculations were performed with a programme developed by Kj. Rasmussen and co-workers[17] and which was further modified to cope with the new empirical potentials.

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

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

where X stands for valence angles around copper when comparing the copper coordination geometry, or the interatomic distance, r, when checking the overall similarity. Δ denotes the difference between the values of the observable X in two structures.

RESULTS AND DISCUSSION

Description of the crystal structure

The molecule in a general orientation is shown in Figure 1. The molecules are mutually connected with two hydrogen bonds [O...O22^i (*i*: $-x, y+1/2, z$) 2.72(1) and O...O12^{ii} (*ii*: $-x, y-1/2, -z$) 2.73(1) Å] forming a polymeric structure of interlocked molecules (Fig. 2). The shortest intermolecular contact is 3.34(1) Å.

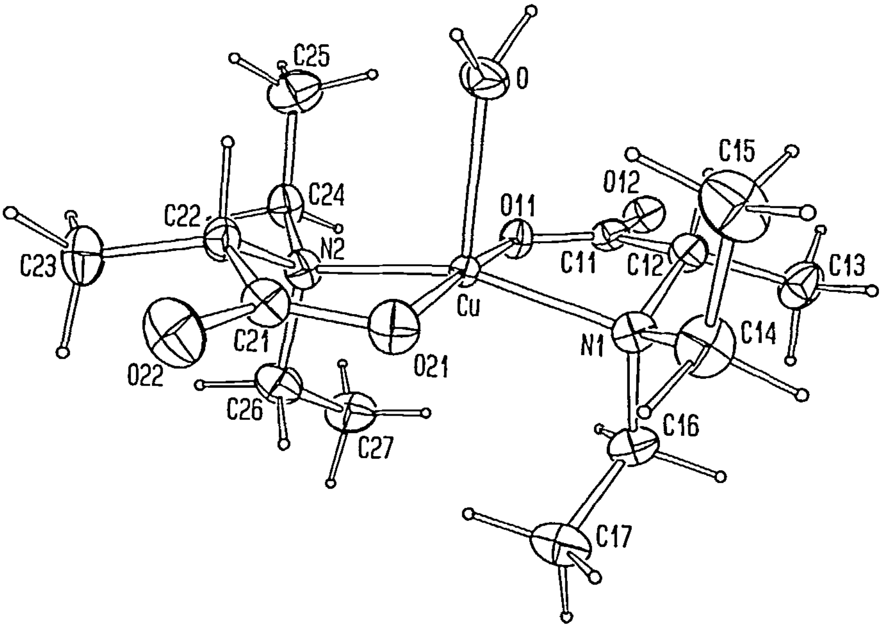

FIGURE 1 Perspective view of the molecule showing the atom numbering scheme and vibrational ellipsoids at the 25% probability level. The hydrogen atoms are drawn at an arbitrary scale.

The coordination sphere around the copper atom is a distorted square pyramid. The apical position of the pyramid is occupied by a water oxygen atom at a surprisngly short distance of 2.263 Å. The amino-acid ligands in the square-pyramidal basal plane are coordinated as bidentates with a *trans* arrangement. The best plane through the four donor atoms showed that copper atom is displaced significantly out-of-plane [0.2383(9) Å] towards the apical water molecule. The nitrogen and oxygen donor atoms themselves appear as a distorted square around the copper. The environment of the copper atom is similar to those found in (*D*-alaninato)(*L*-alaninato)aquacopper(II)[31] and bis(*L*-*N*,*N*-dimethylisoleucinato)aquacopper(II).[24]

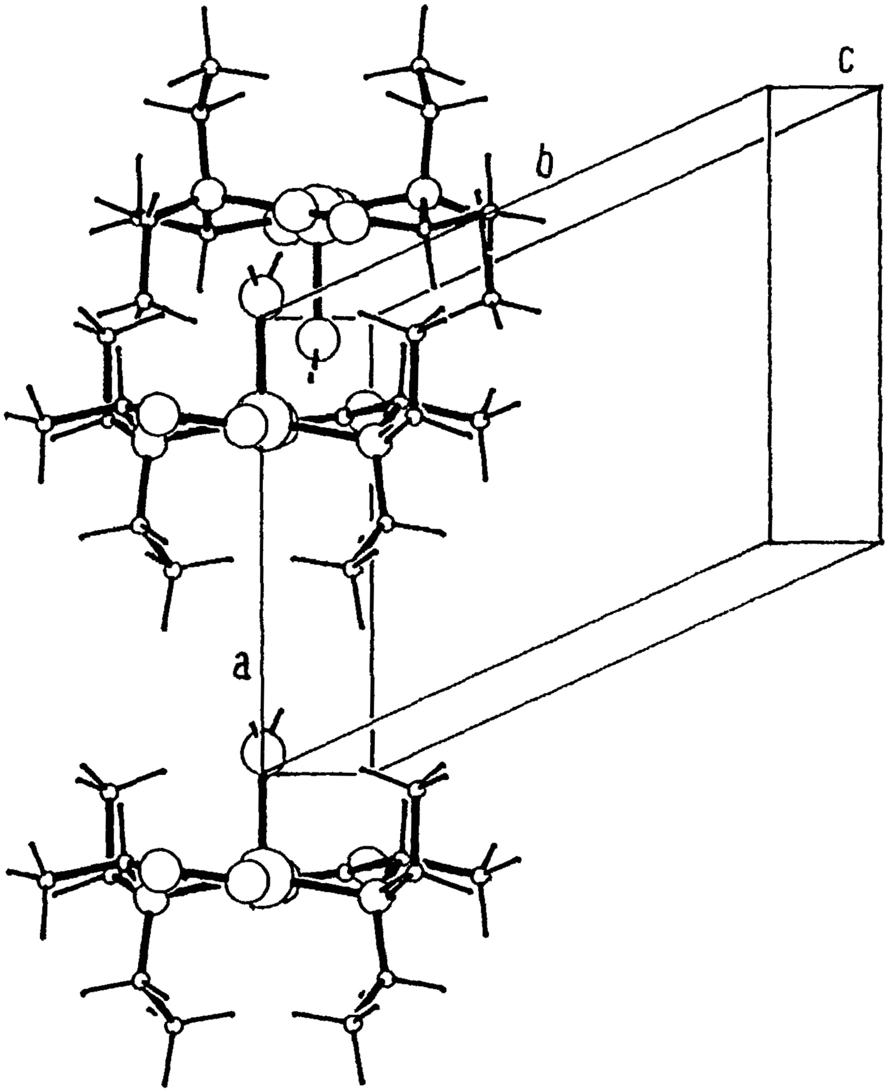

FIGURE 2 Arrangement of the molecules in the crystal lattice of bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) showing the part of polymeric structure formed by hydrogen bonding. Only the most characteristic positions are drawn.

The copper–oxygen bond distances (Table II) are consistent with those in the abovementioned *N*,*N*-dimethylisoleucinato complex (1.900(5) and 1.949(5) Å). These distances cannot be compared to the same ones in other 5- or 6- coordinated copper(II) aminoacidates.[31–34] On the other hand Cu–N distances are remarkably longer in this structure, probably as a consequence of the water molecule (tetragonal distortion).[18,35] The O11–Cu–O21 and N1–Cu–N2 bond angles of 175.7 and 160.0°, respectively, deviate significantly from linearity. All other bond distances and bond angles are consistent with previously reported data.

TABLE II

Internal coordinates of bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) obtained by X-ray analysis and theoretical calculations with two empirical force fields.*

		Theoretical	
Internal coordinate	Experimental	FF2′	FF3′a
Cu–O	2.263(6)	2.481	2.481
Cu–O11	1.899(9)	1.950	1.959
Cu–O21	1.945(9)		
Cu-N1	2.072(6)	2.019	2.025
Cu-N2	2.075(6)		
O11–C11	1.27(1)	1.287	1.283
O21–C21	1.29(1)		
O12–C11	1.23(1)	1.241	1.241
O22–C21	1.24(1)		
N1-C12	1.49(1)	1.489	1.487
N2–C22	1.49(1)		
N1–C14	1.50(1)	1.493	1.493
N2–C24	1.46(1)		
N1-C16	1.51(1)	1.490	1.490
N2-C26	1.53(1)		
C11-C12	1.54(1)	1.530	1.521
C21-C22	1.51(1)		
C12-C13	1.53(1)	1.552	1.551
C22–C23	1.53(1)		
C14–C15	1.50(2)	1.548	1.548
C24–C25	1.51(1)		
C16-C17	1.53(1)	1.548	1.549
C26–C27	1.52(1)		
O–Cu-N1	100.2(2)	98.61	98.40
O–Cu-N2	99.9(2)		
O–Cu–O11	91.9(3)	87.09	85.92
O–Cu–O21	92.3(3)		
O11-Cu-O21	175.7(3)	174.19	171.85
N1-Cu-N2	160.0(3)	162.78	163.20
O11-Cu-N1	83.8(3)	87.33	84.94
O21–Cu-N2	83.9(3)		
O21–Cu-N1	95.3(3)	93.54	96.25
O11-Cu-N2	95.5(2)		

TABLE II (Continued)

Internal coordinate	Experimental	Theoretical	
		FF2′	FF3′a
Cu-O11-C11	116.0(6)	110.69	112.84
Cu-O21-C21	113.5(6)		
Cu-N1-C16	107.3(5)	106.98	106.61
Cu-N2-C26	106.7(5)		
Cu-N1-C14	117.8(5)	116.40	115.14
Cu-N2-C24	118.9(5)		
Cu-N1-C12	101.5(4)	98.89	100.61
Cu-N2-C22	101.9(4)		
C14-N1-C16	107.3(7)	109.76	109.74
C24-N2-C26	108.1(6)		
C12-N1-C16	109.1(7)	110.67	110.87
C22-N2-C26	107.4(6)		
C12-N1-C14	113.4(7)	113.57	113.42
C22-N2-C24	113.2(6)		
O11-C11-O12	126.5(8)	121.07	121.62
O21-C21-O22	122.4(8)		
O12-C11-C12	117.8(7)	123.80	124.33
O22-C21-C22	120.1(7)		
O11-C11-C12	115.5(7)	114.79	114.05
O21-C21-C22	117.4(7)		
N1-C12-C11	108.6(6)	109.33	108.59
N2-C22-C21	109.9(6)		
C11-C12-C13	113.3(7)	111.50	111.67
C21-C22-C23	112.4(7)		
N1-C12-C13	116.1(7)	113.64	113.84
N2-C22-C23	117.8(7)		
N1-C14-C15	113.2(8)	115.14	115.09
N2-C24-C25	114.5(7)		
N1-C16-C17	113.8(7)	112.65	112.64
N2-C26-C27	113.4(8)		
O11-Cu-N1-C14	155.8(7)	151.81	152.77
O21-Cu-N2-C24	155.5(6)		
N1-Cu-O11-C11	−18.5(7)	−9.26	−10.21
N2-Cu-O21-C21	−18.5(6)		

TABLE II (Continued)

Internal coordinate	Experimental	Theoretical	
		FF2′	FF3′a
Cu-O11-C11-C12	−0.7(0)	−15.46	−14.30
Cu-O21-C21-C22	0.4(1.0)		
Cu-N1-C16-C17	−63.6(8)	−60.64	−61.12
Cu-N2-C26-C27	−64.3(8)		
Cu-N1-C14-C15	−65.9(9)	−62.13	−64.12
Cu-N2-C24-C25	−64.3(9)		
Cu-N1-C12-C13	−167.2(6)	−169.10	−169.44
Cu-N2-C22-C23	−167.1(6)		
O11-C11-C12-N1	28.9(1.0)	43.30	41.95
O21-C21-C22-N2	26.9(1.0)		
O12(C11, C12, O11)	−4.4	−5.56	−0.08
O22(C21,C22,O21)	−3.1		

* All distances are expressed in Å and angles in degrees. Standard deviations are given in parentheses. For a description of the force fields see Experimental.

The conformations of both chelate rings are virtually identical (28 pairs of equivalent internal coordinates are identical inside the uncertainty limit of ±2 S.D., 10 are outside the limit, see Table II). The overall conformation of the molecule can be therefore denoted as 1-1LL, according to our notation.[26] Interesting to note, the same conformation of chelate rings was observed in a similar complex, (*D*-*N*,*N*-diethylalaninato)(*L*-*N*,*N*-diethylalaninato)copper(II).[27]

We tried to reproduce the crystal geometry of the molecule with divergent force fields (Fig. 3). The best agreement between crystal and theoretical structures was obtained with "weak" force fields (FF2′, FF2′a and FF3′a), both in terms of overall similarity [$\varepsilon_{r.m.s.}(\Delta r)$] and reproduction of shape of the coordination polyhedron [$\varepsilon_{r.m.s.}(\Delta\theta)$]. Substantially worse results were obtained with the "strong" force field FF1′ and even worse with models which neglected non-bonding interactions with the apically coordinated oxygen atom (FF1–FF3a, M6). The reproduction of the crystal structure with the appropriate force fields is comparable with calculations on the related molecule, bis(*L*-*N*,*N*-dimethylisoleucinato)aquacopper(II).[20] The shape of the coordination polyhedron as observed in crystal and theoretical structures is presented in Figure 4.

Internal coordinates did not reproduce equally well (Table II). The best agreement between experiment and theory was obtained for bond lengths. Only two bond distances (Cu–O and Cu–N1) were outside the range of experimental error, and these two distances—to be noted—were also in contrast with experimental findings on other similar structures (*vide infra*). Less successful was the attempt to reproduce the valence angles (7 successful reproductions of a total of 20) and torsion angles (none

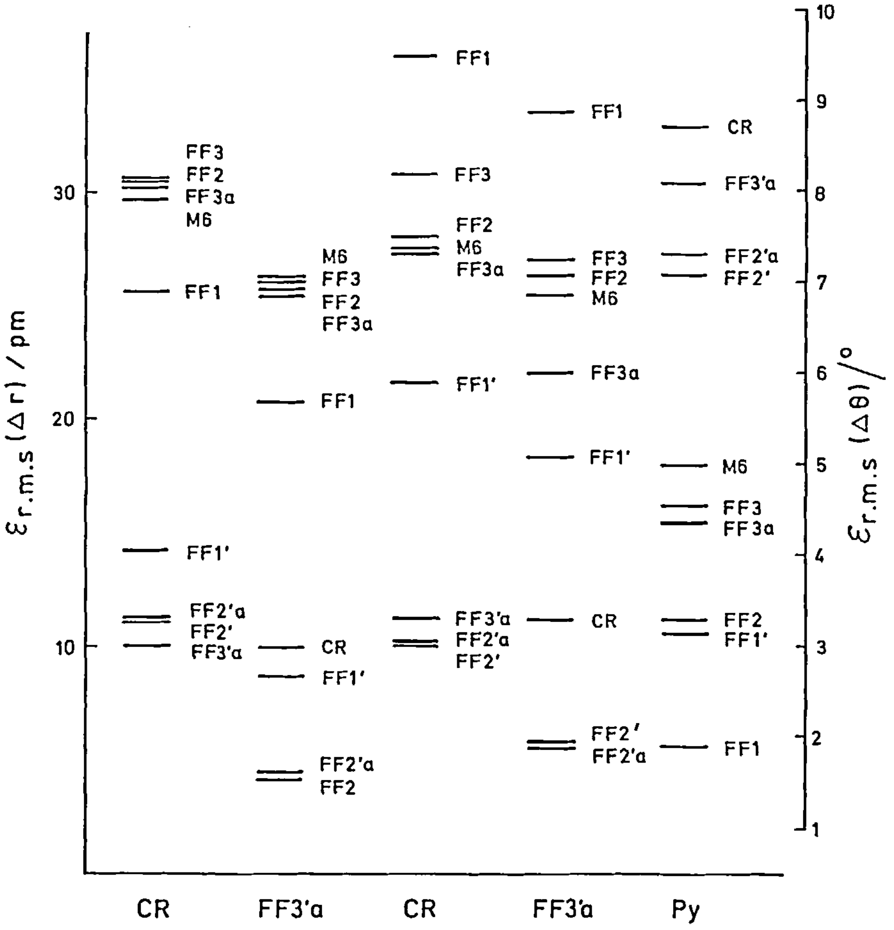

FIGURE 3 Comparison of crystal (CR) and other structures obtained with divergent force fields (FF1, FF2' *etc*) in terms of overall similarity (expressed as $\varepsilon_{r.m.s.}$ (Δr), only non-hydrogen atoms were taken into account) and their ability to reproduce the valence angles around copper ($\varepsilon_{r.m.s}(\Delta\theta)$, all ten angles). Py denotes a square pyramid, the undistorted shape of the coordination polyhedron.

was reproduced inside the limits of experimental error). The worst reproduced were the angles which determined the conformation of the chelate ring (Cu–O11–C11–C12 and O11–C11–C12–N1). Also, the introduction of the V_χ potential (in force fields FF3'a and FF2'a) did not improve agreement between experiment and theory (compare FF3'a with FF3' and FF2'a with FF2'). Even worse, the force field without the V_χ potential (FF2') yielded better values for χ angles than force fields FF3'a (Table II).

Comparison of the coordination polyhedra of bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) obtained experimentally and theoretically (Fig. 3 and Table II) shows that all "weak" force fields yielded similar shapes which are closer to each other than to the crystal structure (*cf* $\varepsilon_{r.m.s.}(\Delta\theta)$ with respect to FF3'a, Fig. 2), but quite different from the polyhedron obtained with the "strong" force field FF1' and from polyhedra obtained by neglecting non-bonding interactions with the apically coordinated water molecule (FF1–FF3a, M6). Comparison of the coordination polyhedra with the "ideal", undistorted configuration (*i.e.* a square pyramid) revealed that the crystal structure was the most distorted from planarity of all structures checked. Also, as expected, apical coordination enhanced the distortion.

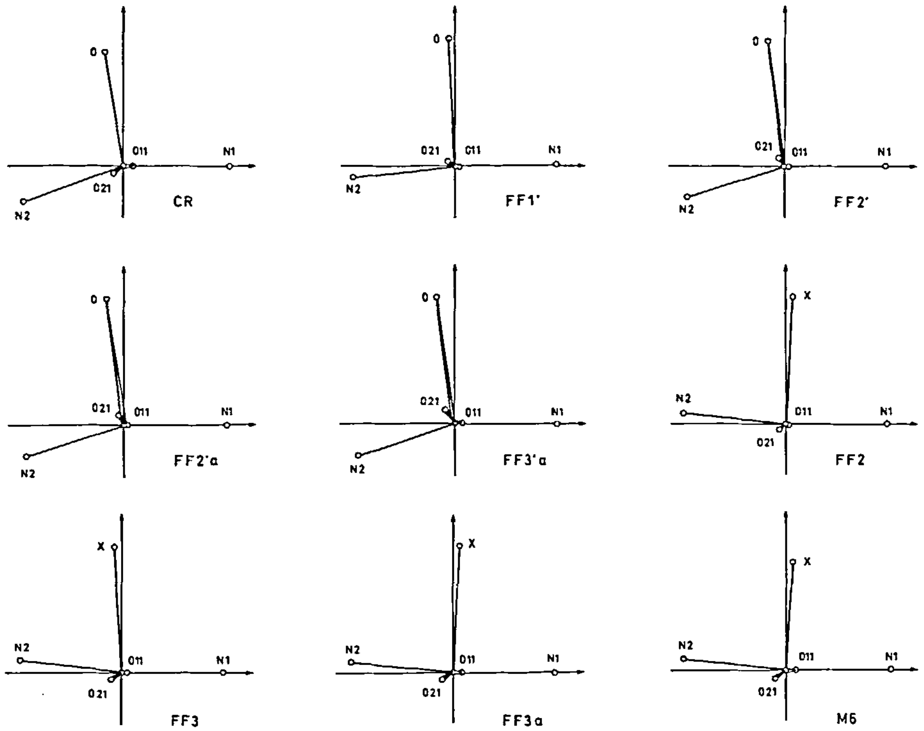

FIGURE 4 The shape of the coordination polyhedron of bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) as observed in the crystal structure (CR) and as obtained with divergent theoretical models. The coordination polyhedra of tetracoordinated bis(*L*-*N*,*N*-diethylalaninato)copper(II) with the same conformation (1–1), obtained with the appropriate theoretical models, are presented for comparison.

Conformational analysis

Bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) has 19 possible conformations of chelate rings[26] and two apical positions for binding the water molecule (on the C^α–H and C^α–CH_3 side of the molecule). It is therefore possible to propose altogether $2 \times 19 \times (19 + 1)/2 = 380$ conformations of the bis complex. To reduce this number, we selected only the conformations of bis(*L*-*N*,*N*-diethylalaninato)-copper(II) which increase their energy up to 500 kJ mol^{-1} upon the placing of the oxygen atom at the apical position (all calculations were done with FF1). As a result of minimization, 17 low-energy conformations were obtained (Table III).

The binding of the water molecule from the C^α–H side of the molecule appears to be to some degree more preferable, especially for conformers with the C^β-equatorial conformation of chelate ring(s) (code number < 11). Also by comparison with the results of conformational analysis of bis(*L*-*N*,*N*-diethylalaninato)copper(II), the binding of water generally increased the difference in energy between the conformers.

TABLE III

Relative conformation energy, V, of the selected conformers of bis(*L*-*N*,*N*-diethylalaninato)aqua-copper(II) obtained with two force fields.*

	$V(\mathrm{kJ\,mol^{-1}})$		
Conformer	FF2′	FF3′a	M6
1 1	3.39^{x}	3.86^{x}	0.47
	7.41	8.05	
1 8	4.77^{x}	5.19^{x}	10.73
1 9	14.32^{x}	16.27^{x}	8.92
1 17	12.46	14.97	8.62
1 18	14.36^{x}	14.20^{x}	0.67
	0.00	1.03	
2 8	19.96^{x}	20.69^{x}	13.63
2 9	12.74^{x}	12.74^{x}	10.23
2 13	16.19^{x}	15.14^{x}	11.31
2 17	8.26^{x}	9.73^{x}	10.31
8 17	13.03	14.60	15.66
8 18	12.65^{x}	12.32^{x}	11.47
	8.20	8.95	
9 18	6.70^{x}	5.84^{x}	7.57
17 17	10.68	11.30	8.47
17 18	12.35	13.07	10.31
18 18	0.82^{x}	0.00^{x}	0.00
	10.27	9.86	

* Conformational potential is expressed relative to the lowest conformer: $V_0 = 38.923\,\mathrm{kJ\,mol^{-1}}$ (FF2′), $V_0 = 35.003\,\mathrm{kJ\,mol^{-1}}$ (FF3′a), $V_0 = 880.260\,\mathrm{kJ\,mol^{-1}}$ (M6). Conformers with the apical water molecule coordinated from the C^{α}–H side of the molecule are denoted by x. All conformers except 1–1 and 18–18 were selected according to the criterion of low steric strain (see text). Conformers of bis(*L*–*N*,*N*-diethylalaninato)copper(II), as obtained with force field M6,[26] were presented for comparison.

As in the case of MLL and MLD isomers of the bis complex of *N*,*N*-diethylalaninato with copper(II),[26] three conformers of bis(*L*,*N*,*N*-diethylalaninato)aqua-copper(II) (1–1^{x}, 1–18 and 18–18^{x}) form a separate group having a distinctively lower strain energy than the rest of conformer population (*cf* Table III). The difference in their energies is substantially higher than for the conformers of bis(*L*-*N*,*N*-diethylalaninato)copper(II), obviously as a consequence of apical ligation.

The most surprising result of conformational analysis is, however, the fact that the conformer observed in the X-ray structure (1–1^{x}) does not correspond to the global minimum of conformational potential (see Table III). In spite of disagreement in conformational energy obtained with diverse force fields (*cf* FF2′ and FF3′a), the fact that conformer 1–1^{x} is about 3–4 $\mathrm{kJ\,mol^{-1}}$ above the global minimum cannot be simply attributed to imprecisions of the molecular mechanics method. More probably the molecular conformation is determined by packing interactions in the crystal lattice. By inspection of molecular models we have found that the arrangement of the molecules having the conformation 1–1^{x} is perfectly suited for the formation of hydrogen bonding as found in the crystal lattice (Fig. 2). This is not true for molecules having the conformation 18–18^{x}. Surprisingly, there are no very close interatomic distances between interlocked molecules of both conformers, but it was found that the orientation of O–H and C=O bonds in conformer 18–18^{x} was not suitable for the formation of the polymeric structure as found in the crystal lattice. From this reasoning, we conclude that the crucial factor which determines the crystal structure (a selection between conformers $1–1^x$ and $18–18^x$) appears to be ring conformation (it has to be noted that $1–1^x$ is the lowest energy conformer with the C^{β}-equatorial conformation, and $18–18^x$ the lowest with the C^{β}-axial conformation)

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SUPPLEMENTARY DATA

Full lists of bond lengths and angles, H atom positions, anisotropic thermal parameters and lists of observed and calculated structure factors are available from the authors.

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