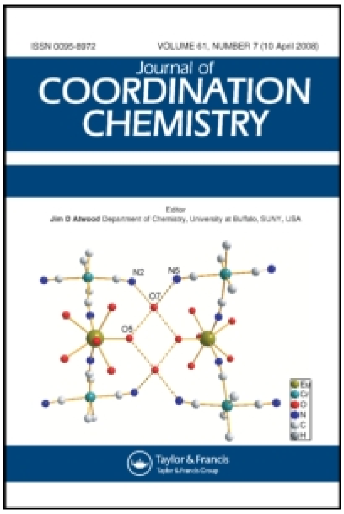

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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

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To cite this Article Kaitner, Branko , Paulić, N. and Raos, N.(1992) 'Stereochemistry of Complexes with *N*-Alkylated Amino Acids. IV. Crystal Structure, Molecular Mechanics Calculations and Conformational Analysis of Bis(*L*-*N*,*N*-Diethyl- α-Alaninato)Aquacopper(II)', Journal of Coordination Chemistry, 25: 4, 337 — 347

To link to this Article: DOI: 10.1080/00958979209409208

URL: http://dx.doi.org/10.1080/00958979209409208

J. Coord. Chem. 1992, Vol. 25, pp. 337–347
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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. IV. CRYSTAL STRUCTURE, MOLECULAR MECHANICS CALCULATIONS AND CONFORMATIONAL ANALYSIS OF BIS(*L*-*N*,*N*-DIETHYL-α-ALANINATO)AQUACOPPER(II)

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(Received October 26, 1990; in final form April 30, 1991)

The crystal structure of the blue orthorhombic (space group $C222_1$) modification of bis(*L*-*N*,*N*-diethyl-α-alaninato)aquacopper was solved by X-ray methods and refined to $R = 0.043$. The complex has twofold crystallographic symmetry and coordination around the copper(II) atom is distorted square-pyramidal with the water molecule axial. Principal dimensions are Cu–Ow 2.260(4), Cu–O 1.922(2), Cu–N 2.075(4) Å, O–Cu–O 175.6(1), N–Cu–N 159.9(2), Ow–Cu–O 92.2(1), Ow–Cu–N 100.0(1)°. The conformation of the unique chelate ring is very similar to that found in (*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

$C_{14}H_{30}CuN_2O_5$, $M_r = 369.95$, orthorhombic, space group $C222_1$, $a = 8.249(1)$, $b = 18.695(3)$, $c = 11.455(2)$ Å, $V = 1766.5(5)$ Å^3, $Z = 4$, $D_x = 1.391$ g cm^{-3}, $F(000) = 788$, $\lambda(\mathrm{MoK}\alpha) = 0.7107$ 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 $C222_1$. A total of 1665 reflections ($\theta < 27°$; $\theta/2\theta$ scan) 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. The 1418 reflections with $I > 2.5\,\sigma(I)$ were used in the subsequent structure analysis. The structure was solved by the heavy-atom method. The complex has two-fold crystallographic symmetry with the copper atom and water molecule on the two-fold axis. Refinement was carried out by full-matrix least-square methods based on F. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were visible as clear maxima in a difference Fourier map and were included as riding atoms in the structure factor calculations in their expected geometric positions. Convergence was reached at $R = 0.043$, $wR = 0.044$, $w = 1/\sigma^2 F_o$, $S = 1.14$, $(\Delta/\sigma)_{max} = 0.009$, $\Delta\rho_{max.min} = \pm 0.49\,e\text{Å}^{-3}$. 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] All calculations were performed with NRCVAX[30] on a 386/33 MHz personal computer.

TABLE I

Final fractional coordinates ($\times 10^4$, $\times 10^5$ for Cu) and equivalent isotropic thermal parameters B_{eq} (Å^2) with e.s.d.'s in parentheses.

	x/a	y/b	z/c	B_{eq}
Cu	22696(8)	0	0	2.49(3)
Ow	−470(5)	0	0	4.5(3)
O1	2359(3)	−18(3)	−1677(2)	3.4(2)
O2	2099(5)	670(2)	−3235(3)	4.2(2)
N	2707(5)	1084(2)	−230(3)	2.9(2)
C1	2174(6)	585(3)	−2172(4)	2.9(2)
C2	1901(6)	1220(3)	−1376(4)	3.1(2)
C3	2289(8)	1930(3)	−1966(5)	4.4(3)
C4	2183(7)	1578(3)	705(5)	4.1(2)
C5	364(8)	1607(3)	874(6)	5.6(3)
C6	4526(7)	1173(3)	−381(6)	4.1(3)
C7	5510(8)	956(4)	673(6)	5.2(3)

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

Conformational analysis

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

$$V = 1/2 \sum_{i} k_{b,i}(b_i - b_{o,i})^2 + 1/2 \sum_{j} k_{\theta,j}(\theta_j - \theta_{o,j})^2 + 1/2 \sum_{k} V_n(1 \pm \cos n\varphi_k) +$$

$$\sum(A_l \exp(-B_l r_l) - C_l r_l^{-6}) + 1/2 \sum_{m} k_{\chi,m}\chi_m^2 + 1/2\, k_\beta(\beta - \beta_o)^2 + V_{cis} + V_{trans} + V_{el} \qquad (1)$$

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 linked by O–H...O hydrogen bonds [Ow–H...O2** (**: $-x, y, -1/2 - z$) and Ow–H...O2*** (***: $-x, -y, 1/2 + z$) 2.7318 Å] forming a polymeric structure of interlocking molecules. All other intermolecular contacts correspond to van der Walls interactions.

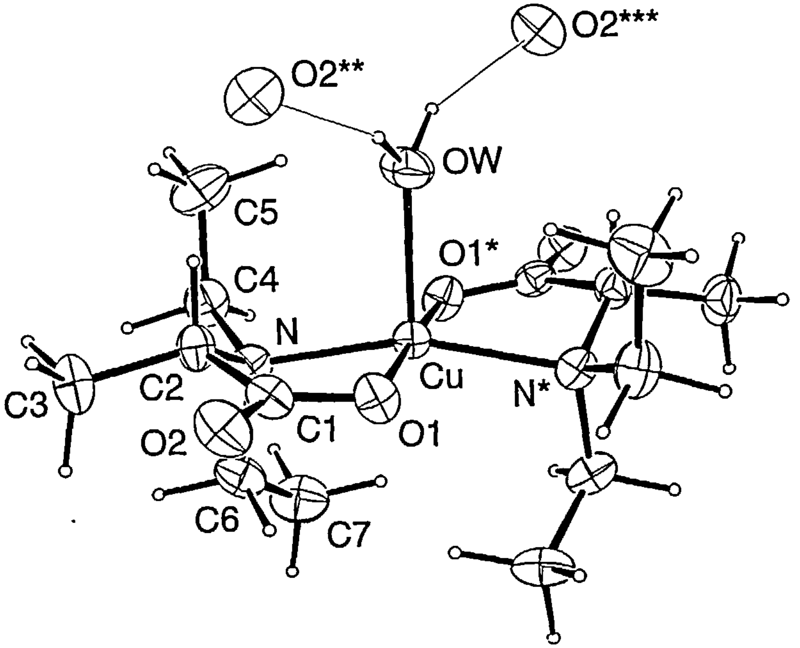

FIGURE 1 Perspective view of the molecule showing the crystallographic numbering scheme. The vibrational ellipsoids are at the 35% probability level. The hydrogen atoms are drawn at an arbitrary scale. The codes for symmetry related atoms are: (*) $x, -y, -z$; (**) $-x, y, -1/2 - z$; (***) $-x, -y, 1/2 + z$.

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 the surprisingly short distance of 2.260(4) 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 the copper atom is displaced significantly out of plane [0.245(2) 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]

The Cu–O bond distance 1.922(2) Å (Table II) is intermediate between those in the above mentioned *N*,*N*-dimethylisoleucinato complex [1.900(5) and 1.949(5) Å]. In other 5- and 6-coordinated copper(II) aminoacidates corresponding Cu–O distance is longer with an average value of 1.953(4) Å.[31–34] On the other hand the Cu–N distance is remarkably longer in this structure, probably as a consequence of the water molecule approaching the copper atom (tetragonal distortion).[18,35] The

O1-Cu-O1*, 175.6(1)°, and N-Cu-N*, 159.9(2)°, bond angles deviate significantly from linearity. All other bond distances and bond angles are consistent with previously reported data.

TABLE II

Summary of the values of bond distances, bond angles and torsion angles (internal coordinate) of bis-(*L-N,N*-diethylalaninato)aquacopper(II) obtained by X-ray analysis and theoretical calculations with two empirical force fields.*

Internal coordinate and out-of-plane angle	Experimental	Theoretical	
		FF2′	FF3′a
Cu-OW	2.260(4)	2.481	2.481
Cu-O1	1.922(2)	1.950	1.959
Cu-N	2.075(4)	2.019	2.025
O1-C1	1.272(7)	1.287	1.283
O2-C1	1.230(5)	1.241	1.241
N-C2	1.494(6)	1.489	1.487
N-C4	1.479(6)	1.493	1.493
N-C6	1.519(7)	1.490	1.490
C1-C2	1.513(7)	1.530	1.521
C2-C3	1.524(7)	1.552	1.551
C4-C5	1.514(9)	1.548	1.548
C6-C7	1.511(9)	1.548	1.549
OW-Cu-N1	100.0(1)	98.61	98.40
OW-Cu-O1	92.2(1)	87.09	85.92
O1-Cu-O1(i)	175.6(1)	174.19	171.85
N-Cu-N(i)	159.9(2)	162.78	163.20
O1-Cu-N	83.4(2)	87.33	84.94
O1-Cu-N(i)	95.5(2)	93.54	96.25
Cu-O1-C1	115.2(3)	110.69	112.84
Cu-N-C6	107.1(3)	106.98	106.61
Cu-N-C4	117.8(3)	116.40	115.14
Cu-N-C2	101.5(3)	98.89	100.61
C4-N-C6	107.6(4)	109.76	109.74
C2-N-C6	108.7(3)	110.67	110.87
C2-N-C4	113.6(4)	113.57	113.42
O1-C1-O2	124.3(4)	121.07	121.62
O2-C1-C2	119.2(4)	123.80	124.33
O1-C1-C2	116.4(4)	114.79	114.06
N-C2-C1	109.3(4)	109.33	108.59
C1-C2-C3	112.7(4)	111.50	111.67
N-C2-C3	116.4(4)	113.64	113.84
N-C4-C5	113.9(5)	115.14	115.09
N-C6-C7	114.2(4)	112.65	112.64
O1-Cu-N-C4	155.6(3)	151.81	152.77
N-Cu-O1-C1	−18.5(2)	−9.26	−10.21
Cu-O1-C1-C2	−0.4(2)	−15.46	−14.30
Cu-N-C6-C7	−63.4(3)	−60.64	−61.12
Cu-N-C4-C5	−64.9(3)	−62.13	−64.12
Cu-N-C2-C3	−166.9(4)	−169.10	−169.44
O1-C1-C2-N	28.5(3)	43.30	41.95
O2(C1,C2,O1)	−4.1	−5.56	−0.08

* 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; (i) refers to the equivalent position x, $-y$, $-z$.

The overall conformation of the molecule is denoted as 1-1LL, according to our notation.[26] Interestingly, 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, Figure 2. The best agreement between experiment and theory was obtained for bond lengths. Less successful was the attempt to reproduce the valance angles and torsion angles.

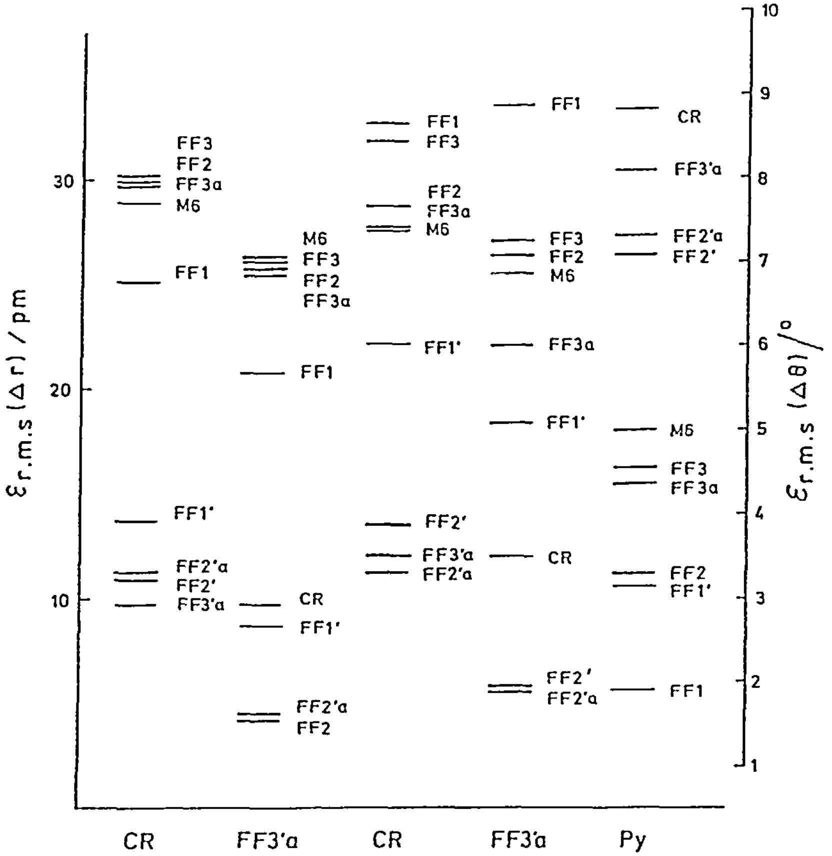

FIGURE 2 Comparison of crystal (CR) and other structures obtained with divergent force fields (FF1, FF2′ *etc*) in terms of overall similarity (expressed as $\varepsilon_{r.m.s.}$ (Δr), only non-hydrogen atoms were taken into account) and their ability to reproduce the valence angles around copper ($\varepsilon_{r.m.s.}$(Δθ), all ten angles). Py denotes a square pyramid, the undistorted shape of the coordination polyhedron.

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 3.

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–N) 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 was reproduced inside the limits of experimental error). The worst reproduced were the angles which determined the conformation of the chelate ring (Cu–O1–C1–C1 and O1–C1–C1–N). Also, the introduction of the V potential (in force fields FF3′a and FF2′a) did not improve agreement between experiment and theory (compare FF3′a with FF2′ and FF2′a with FF2′). Even worse, the force field without the V potential (FF2′) yielded better values for angles than force fields FF3′a (Table II).

Comparison of the coordination polyhedra of bis(*L*-*N*,*N*-diethylalaninato)aqua-copper(II) obtained experimentally and theoretically (Fig. 2 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), 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 coordinated 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.

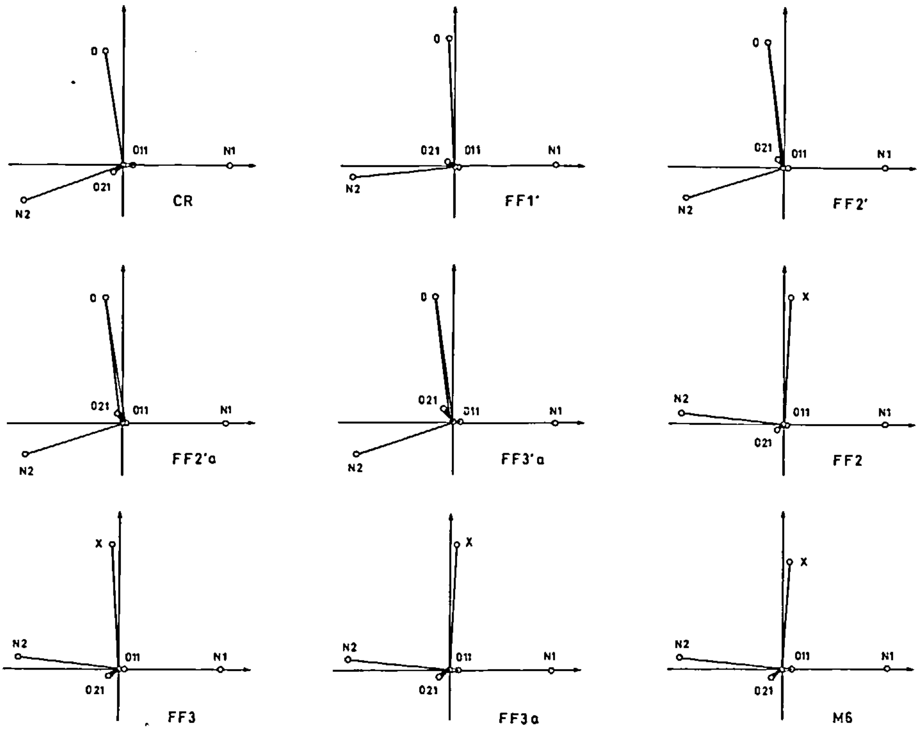

FIGURE 3 The shape of the coordination polyhedron of bis(*L*-*N*,*N*-diethylalaninato)aquacopper(II) as observed in the crystal structure (CR) and as obtained with divergent theoretical models. The coordination polyhedra of tetracoordinated bis(*L*-*N*,*N*-diethylalaninato)copper(II) with the same conformation (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(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: $V_o = 38.923$ kJ mol^{-1} (FF2′), $V_o = 35.003$ kJ mol^{-1} (FF3′a), $V_o = 880.260$ 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 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).

ACKNOWLEDGEMENTS

We thank Professor G. Ferguson, Chemistry Department, University of Guelph for helpful discussion, NSERC Canada for a visiting professorship (to BK), and Dr. Kj. Rasmussen for allowing us to use his computer programme for conformational analysis (NR). The Republican (Zagreb, Croatia) and Federal (Belgrade) Foundations for Scientific Research are gratefully acknowledged.

SUPPLEMENTARY DATA

Tables of bond lengths and bond angles, torsion angles, H atom coordinates, anisotropic thermal parameters, least-squares planes and lists of observed and calculated structure factors are available from the Editor on request.

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