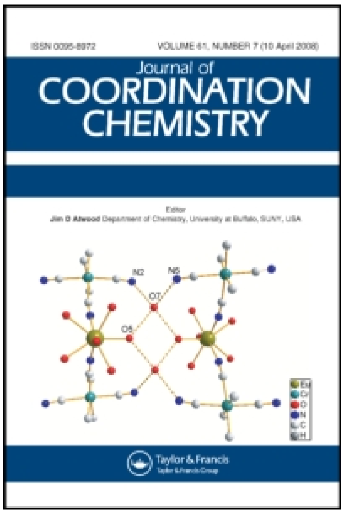

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. IX. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF AQUA*BIS* (*L*-*N*-BENZYLALANINATO)COPPER(II) MONOHYDRATE

B. Kaitner[a]; E. Meštrović[a]; N. Paulić[b]; N. Raos[b]
[a] Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia [b] Institute for Medical Research and Occupational Health, Zagreb, Croatia

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. IX. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF AQUA*BIS* (*L*-*N*-BENZYLALANINATO)COPPER(II) MONOHYDRATE

B. KAITNER, E. MEŠTROVIĆ

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

N. PAULIĆ and N. RAOS*

Institute for Medical Research and Occupational Health, Zagreb, Croatia

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The structure of a blue, monoclinic (space group $P2_1$) crystal of aqua*bis*(*L*-*N*-benzylalaninato) copper(II) monohydrate was determined by X-ray diffraction methods and refined to $R = 0.027$. The structure consists of discrete molecules linked together by O-H—O and N-H—O hydrogen bonds. The coordination around the copper(II) atom is distorted square-pyramidal with alanine N and O atoms in *trans* orientations. The O-Cu-OW, O-Cu-N and OW-Cu-N bond angles range from 83.48(8)° to 96.33(8)°. Values for O-Cu-O and N-Cu-N are 173.87(9)° and 165.47(9)°, respectively. The shape of the coordination polyhedron was reasonably well reproduced with molecular mechanics calculations, yielding root-mean-square deviations of ten valence angles around copper to 3.7°. The calculated strain energy of the crystal conformation is 23 kJ mol^{-1} higher than the energy of the most stable conformer. This is attributed to additional stabilization of molecular conformation by intermolecular interactions in the solid state.

KEYWORDS: aqua*bis*(*N*-benzylalaninato)copper(II), copper, X-ray structure, conformational analysis, molecular mechanics

INTRODUCTION

Copper(II) chelates with *N*-alkylated and *N,N*-dialkylated α-amino acids[1] appear to be, due to extensive steric strain originating from the close contacts of bulky groups, nearly ideal model compounds for a study of the distortion of the copper(II) coordination polyhedron. These compounds form three basic crystal modifications: (1) a red modification with planar, usually *trans*, arrangement of two chelate rings,

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* Author for correspondence.

(2) a blue modification with apical coordination of a ligand water or carboxylate oxygen of a neighbouring molecule and (3), a very rare, green modification with an "acetato-like" structure.

In our laboratory we have developed molecular mechanics models for simulation of the distortion of the copper(II) coordination polyhedron. Simple "dummy" atom models[2] appear suitable for calculations involving aqua-complexes (blue modification),[3–6] but not for the red modification. To solve the latter problem, two new kinds of models were developed: (1) a model with the distortion coordinate defined as an angle between the bisectors of two opposite valence angles in chelate rings[7–9] and (2) models with the coulombic potential between charges situated on atoms in the coordination plane and two charges below and above the plane.[10,11] Model with the coulombic potential proved best for reproducing the geometry of the copper(II) coordination polyhedron[12] but there were only slight differences among the models in successfully reproducing the enantioselectivity observed in the copper(II)/*N,N*-dimethylvalinate systems.[7,8,10,13]

The concern of this paper is a conformational study of aqua*bis*(*L*-*N*-benzylalaninato)copper(II). Molecular mechanics calculations have to answer two specific questions. First, are the molecular mechanics models suitable, and to what extent, in reproducing the exact geometry of copper(II) coordination polyhedron. Secondly, is the conformation of the molecule, as observed in the crystal state, determined also with intermolecular interactions, *i.e.*, does the crystal conformation correspond to the lowest (global) energy minimum of the conformational potential. The answer to those questions would throw more light on one specific problem of copper (II) stereochemistry — the plasticity of the copper(II) coordination sphere.[14]

EXPERIMENTAL

The ligand, *L*-*N*-benzylalanine (m.p. 255°C) was prepared by condensation of *L*-alanine with benzaldehyde and subsequent reduction with $NaBH_4$.[15] The product was characterized by mass spectroscopy. The complex was prepared by reaction of the ligand and copper(II) acetate monohydrate in CH_2Cl_2 solution.[16] Crystals were obtained from ethanol solution by slow evaporation.

Crystal structure determination

Crystal data: $C_{20}H_{28}CuN_2O_6$, $M_r = 455.99$, monoclinic, space group $P2_1$, $a = 7.315(2)$, $b = 10.880(4)$, $c = 14.188(5)$Å, $\beta = 104.72(3)°$, $V = 1092.1(7)$Å^3, $Z = 2$, $D_x = 1.387$ g cm^{-3}, F (000) = 478, λ(Mo*Kα*) = 0.7093Å, μ(Mo*Kα*) = 10.4 cm^{-1}.

A blue prism-shaped crystal of dimensions 0.71 × 0.55 × 0.33 mm was used for data collection on a Philips PW 1100 (Stoe upgrade) diffractometer with graphite-monochromated Mo*Kα* radiation. Lattice parameters deviations were derived from the setting angles of 22 reflections with $16° < 2\theta < 27°$. A total of 5011 intensity maxima and their Friedel pairs was collected in the range $4° < 2\theta < 54°$ using the ω scan technique. After merging of equivalent reflections ($R_{\text{int}} = 0.042$) there remained 4156 unique data with $I \geq 3\sigma(I)$. These reflections along with their Friedel pairs were considered as being observed and were used in structure solution and refinement, and in anomalous dispersion assignment of absolute configuration. The *hkl* range was − 9 to 9, 0 to 13, and 0 to 18, respectively. Three standard reflections monitored periodically throughout the data collection showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarization effects.[17] Empirical absorption corrections were applied using *DIFABS*[18] with transmission factors $t_{\mathrm{min}} = 0.828$ and $t_{\mathrm{max}} = 1.116$. The structure was solved using the Patterson method to locate the Cu atom. Successive Fourier syntheses provided the positions of all remaining non-H atoms. Coordinates of all hydrogen atoms were calculated for geometrically expected positions with d(N-H) = 1.00 Å and d(C-H) = 0.95 Å; the water molecule hydrogen atoms were found in a difference Fourier map, and included in the structure factor calculation only. The absolute configuration was established unequivocally by refinement of a δf'' multiplier.[19] The refinement of non-hydrogen atoms was by full-matrix least-squares methods. Final residuals were $R = 0.027$, $R_w = 0.038$, S = 1.12 for 261 variable parameters with $w = 1/(\sigma^2 F_o + 0.0008F_o^2)$. In the last ΔF-map the deepest hole was − 0.44 e/Å^3, and the highest peak 0.30 e/Å^3. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[20] All calculations were performed with the *NRCVAX*[21] suite of programs. Table 1 lists final atomic coordinates along with the equivalent isotropic thermal parameters and Table 2 gives crystallographic and theoretical (based on molecular mechanics calculations) bond lengths, valence angles and selected torsion angles.

Table 1 Final atomic fractional coordinates (× 10^4, × 10^5 for Cu) and equivalent isotropic temperature factors B_{eq} (Å^2)

	x/a	*y/b*	*z/c*	B_{eq}*
Cu	76196(3)	0	92426(2)	2.81(1)
O11	9593(2)	1205(2)	9289(1)	3.5(1)
O12	11578(3)	1938(2)	8493(2)	5.3(1)
O21	5466(2)	-1055(2)	9163(1)	3.9(1)
O22	3626(2)	-1867(2)	10028(1)	3.7(1)
OW1	9693(3)	-1604(2)	9643(2)	4.3(1)
OW2	5113(3)	1966(2)	8038(2)	5.5(1)
N1	7589(2)	-94(2)	7815(1)	3.0(1)
N2	7258(2)	477(2)	10552(1)	2.6(1)
C11	10298(3)	1247(2)	8550(2)	3.4(1)
C12	9456(4)	352(2)	7718(2)	3.8(1)
C13	9433(7)	914(5)	6742(2)	7.7(2)
C14	6966(4)	-1289(2)	7336(2)	3.6(1)
C15	6270(4)	-1258(3)	6244(2)	3.7(1)
C16	4895(5)	-448(3)	5766(2)	5.3(1)
C17	4242(6)	-500(5)	4755(3)	7.2(2)
C18	4932(8)	-1343(5)	4233(3)	7.6(2)
C19	6261(8)	-2129(5)	4689(3)	7.6(2)
C110	6948(5)	-2112(3)	5692(2)	5.2(1)
C21	4864(3)	-1132(2)	9922(2)	3.0(1)
C22	5721(3)	-278(2)	10765(2)	2.9(1)
C23	4198(4)	498(4)	11024(3)	6.2(2)
C24	9037(3)	429(2)	11336(2)	3.3(1)
C25	8806(3)	852(3)	12314(2)	3.3(1)
C26	8255(4)	2036(3)	12429(2)	4.3(1)
C27	7987(5)	2433(4)	13311(3)	5.7(2)
C28	8272(5)	1667(6)	14077(2)	7.0(2)
C29	8824(6)	475(5)	13985(2)	6.9(2)
C210	9110(4)	58(4)	13101(2)	5.2(1)

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

Table 2 Interatomic distances (Å), valence angles (°) and selected torsion angles (°).

Internal coordinate	Experimental value	Theoretical value (FF3′a)
Cu-O11	1.939(2)	1.949
Cu-O21	1.929(2)	1.949
Cu-OW1	2.287(2)	2.477
Cu-N1	2.022(2)	2.012
Cu-N2	2.010(2)	2.012
O11-C11	1.281(3)	1.277
O21-C21	1.265(3)	1.277
O12-C11	1.219(3)	1.241
O22-C21	1.246(3)	1.241
N1-C12	1.489(3)	1.482
N2-C22	1.484(3)	1.482
N1-C14	1.484(3)	1.483
N2-C24	1.483(3)	1.483
C11-C12	1.533(4)	1.520
C21-C22	1.519(3)	1.520
C12-C13	1.510(4)	1.552
C22-C23	1.516(4)	1.552
C14-C15	1.504(4)	1.521
C24-C25	1.511(3)	1.521
C15-C16	1.379(4)	1.407
C25-C26	1.372(4)	1.407
C15-C110	1.385(4)	1.408
C25-C210	1.385(4)	1.408
C16-C17	1.393(5)	1.405
C26-C27	1.383(4)	1.406
C17-C18	1.355(8)	1.405
C27-C28	1.344(7)	1.405
C18-C19	1.332(9)	1.405
C28-C29	1.374(8)	1.405
C19-C110	1.384(6)	1.406
C29-C210	1.399(5)	1.406
O11-Cu-O21	173.87(9)	167.82
O11-Cu-OW1	93.80(8)	96.09
O21-Cu-OW1	92.32(9)	96.09
O11-Cu-N1	83.48(8)	86.33
O21-Cu-N2	84.86(8)	86.33
O11-Cu-N2	93.78(8)	92.48
O21-Cu-N1	96.33(8)	92.48
OW1-Cu-N1	92.78(9)	95.63
OW1-Cu-N2	101.65(8)	95.64
N1-Cu-N2	165.47(9)	168.73
Cu-O11-C11	116.6(2)	119.0
Cu-O21-C21	114.4(2)	111.9
Cu-N1-C12	107.4(1)	107.1
Cu-N2-C22	109.3(1)	107.1
Cu-N1-C14	115.3(2)	109.0
Cu-N2-C24	112.8(1)	109.0
C12-N1-C14	115.1(2)	112.8
C22-N2-C24	113.1(2)	112.8
O11-C11-O12	123.5(2)	118.4
O21-C21-O22	124.5(2)	118.4
O11-C11-C12	116.2(2)	120.1
O21-C21-C22	117.8(2)	120.1
O12-C11-C12	120.4(2)	121.4

Table 2—(*Continued*)

Internal coordinate	Experimental value	Theoretical value (FF3′a)
O22-C21-C22	117.7(2)	121.4
N1-C12-C11	109.5(2)	108.9
N2-C22-C21	111.1(2)	108.9
N1-C12-C13	114.9(3)	111.3
N2-C22-C23	112.5(2)	111.3
C11-C12-C13	111.0(3)	110.5
C21-C22-C23	110.5(2)	110.5
N1-C14-C15	115.9(2)	111.8
N2-C24-C25	113.4(2)	111.8
C14-C15-C16	122.3(3)	119.6
C24-C25-C26	120.0(2)	119.6
C14-C15-C110	119.4(3)	120.8
C24-C25-C210	121.2(3)	120.8
C16-C15-C110	118.2(3)	119.6
C26-C25-C210	118.7(3)	119.6
C15-C16-C17	119.8(3)	120.2
C25-C26-C27	121.0(3)	120.2
C16-C17-C18	120.8(4)	120.0
C26-C27-C28	120.6(4)	120.0
C17-C18-C19	119.7(3)	119.9
C27-C28-C29	119.8(3)	119.9
C18-C19-C110	121.4(4)	120.0
C28-C29-C210	120.4(4)	120.0
C15-C110-C19	120.1(4)	120.2
C25-C210-C29	119.4(4)	120.2
Cu-N1-C14-C15	158.9(2)	178.1
Cu-N2-C24-C25	176.9(2)	178.1
Cu-N1-C12-C13	-152.4(2)	- 146.0
Cu-N2-C22-C23	-126.5(2)	-145.9
Cu-O11-C11-C12	1.1(1)	-11.3
Cu-O21-C21-C22	7.4(1)	-11.2
N1-Cu-O11-C11	-13.9(1)	-3.3
N2-Cu-O21-C21	-6.8(1)	-3.3
O11-Cu-N1-C14	152.3(2)	138.3
O21-Cu-N2-C24	131.3(1)	138.3
O11-C11-C12-N1	18.1(1)	24.8
O21-C21-C22-N2	-3.3(1)	24.8
N1-C14-C15-C16	-52.0(2)	-79.2
N2-C24-C25-C26	-62.2(2)	-79.2
C14-C15-C16-C17	-177.0(4)	179.2
C24-C25-C26-C27	178.3(3)	179.2
C14-C15-C110-C19	177.3(4)	-179.1
C24-C25-C210-C29	-178.0(4)	-179.1
C15-C16-C17-C18	0.4(2)	0.4
C25-C26-C27-C28	0.3(2)	0.4
C16-C17-C18-C19	-0.4(2)	0.4
C26-C27-C28-C29	-0.3(2)	0.4
C17-C18-C19-C110	0.6(2)	-0.3
C27-C28-C29-C210	0.6(2)	-0.3
C18-C19-C110-C15	-0.7(2)	-0.6
C28-C29-C210-C25	-0.9(2)	-0.6

Conformational analysis

The conformational potential (or strain energy) was calculated from (*1*),

$$\Phi_T = \frac{1}{2}\sum_i k_{d,i}(d_i - d_{o,i})^2 + \frac{1}{2}\sum_j (\theta_j - \theta_{o,j})^2 + \frac{1}{2}\sum_k \Phi_n(1 \pm \cos n\gamma_k) + \sum_l (A_l \exp(-B_l r_l) - C_l r_l^{-6}) + \frac{1}{2}\sum k_{\chi,m}\chi_m^2 \qquad (1)$$

where d, θ, γ and χ stand for bond lengths, valence, torsion and out-of-plane angles, respectively; r is a non-bonded distance. K_d is an empirical parameter for bond stretching and k_θ for valence angle bending. Torsion interactions were determined with parameters Φ_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 carboxyl groups and benzene ring with a quadratic function dependent on parameter k_χ (= 100 kcal mol^{-1} rad^{-2}) was also taken into account.

The calculations were carried out with the "dummy" atom model; in force fields denoted with a prime, interactions with the apical water (having the same parameters as oxygen) were also taken into account. Parameters for copper are given elsewhere:[22] the rest of the parameters are reported in ref. 2 and for the aromatic part of the molecule in ref. 23. Calculations were performed with a program developed by Kj. Rasmussen and coworkers.[24]

Root-mean-square deviations were calculated from (*2*),

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

where X stands for either valence angles (θ) or interatomic distances (r) while Δ denotes the difference between the observed and calculated value of observable X.

RESULTS AND DISCUSSION

The compound crystallizes as an aqua complex with two water molecules in the asymmetric unit. The structure consists of discrete molecules linked together by O-H–O and N-H–O hydrogen bonds. An *ORTEP*II[25] view of the molecule in a general orientation and the pattern of the hydrogen bonds in the structure are displayed in Figure 1. The copper atom coordination polyhedron is an irregular square pyramid having a water molecule in the apical position and two oxygen and two nitrogen atoms in *trans* positions in the equatorial plane. The metal atom is displaced 0.166Å out of the mean plane comprising O11, O21, N1 and N2 towards water molecule OW1. In the series of analogous copper complexes with *N*-alkylated amino acids, only certain similarity in the molecular geometry of the copper environment is observed.[3-6,22,26,27] The Cu-OW bond length 2.287(2)Å is close to the value of 2.260(4)Å found in the aqua*bis*(*N*,*N*-diethylalaninato) derivative,[4] although there is a shorter Cu-OW bond distance, 2.206(3)Å, in the aqua*bis*(*N*,*N*-dimethylthreoninato) complex.[6] Taking the 3σ criterion into account, there are two almost identical copper-water bond in the aqua*bis*(*N*,*N*-dimethylisoleucinato)[3] and aqua*bis*(*N*-*tert*-butyl-*N*-methylglycinato)[5] compounds [2.448(6)Å and 2.464(2)Å,

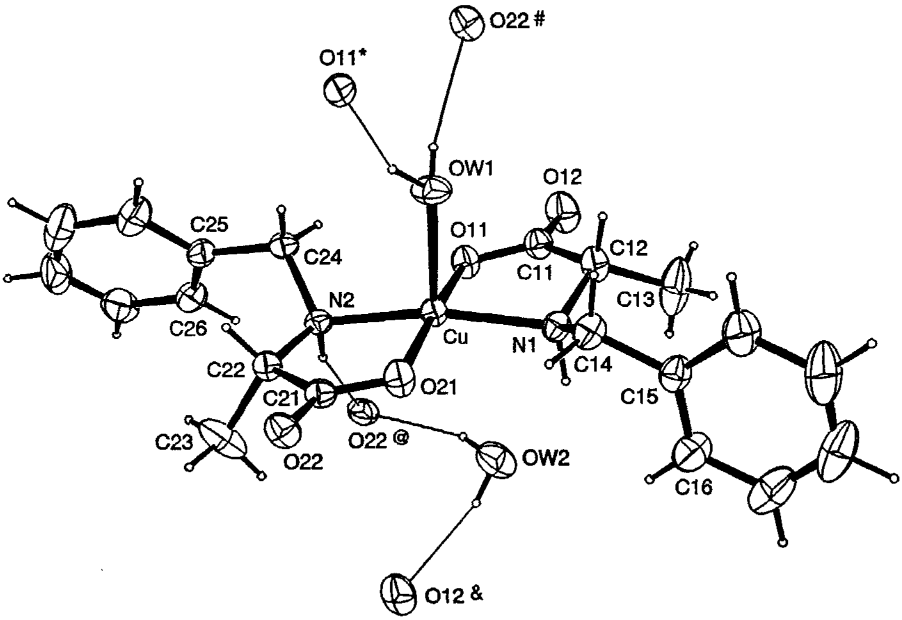

Figure 1 A perspective view of aqua*bis(L-N*-benzylalaninato)copper (II) monohydrate showing the crystallographic numbering scheme. Vibrational ellipsoids are drawn at the 30% probability level. Open circles represent hydrogen atoms of arbitrary radius. The codes for symmetry related atoms included in hydrogen bonding are: (*) $-x+2$, $y-0.5$, $-z+2$; (#) $x+1$, y, z; (&) $x-1$, y, z; (@) $-x+1$, $y+0.5$, $-z+2$.

respectively]. Cu-OW bond distances are probably influenced by the four different amino acids (alanine, threonine, isoleucine and glycine) and *N*-substitution by different radicals (methyl, ethyl, *tert*-butyl and benzyl), although conformation of the molecules and crystal packing (isolated discrete or molecules linked through hydrogen bonding) must be taken into account as well. The observed Cu-O [1.929(2)Å, 1.939(2)Å] and Cu-N [2.010(2)Å, 2.022(2)Å] distances are between the values of Cu-O$_{\text{min}}$ 1.900(5)Å and Cu-O$_{\text{max}}$ 1.949(5)Å [aqua*bis*(*N,N*-dimethylisoleucinato) complex][3] and Cu-N$_{\text{min}}$ 2.007(4) [*bis*(*N,N*-dimethylisoleucinato) complex][22] and 2.112(3)Å [aqua*bis*(*N,N*-dimethylthreoninato) complex].[27] Distortion of the square pyramid is considerable with respect to bond angles. O-Cu-OW, O-Cu-N and OW-Cu-N bond angles range from 83.48(8)° to 96.33(8)°. Values for O-Cu-O and N-Cu-N are 173.87(9)° and 165.47(9)°, respectively showing the large deviation from linearity characteristic of all of the abovementioned aqua-compounds. There are essential differences in the conformations of the two chelate rings. One of them (chelate ring 2) is almost planar with the largest deviation being 0.056(3)Å for O21 from the best plane through Cu, O21, C21, C22 and N2. The other chelate ring (1) has the open envelope conformation with the Cu-O11-C11-C12 torsion angle 1.1(1)° and N1 deviating from the Cu, O11, C11, C12 mean plane by 0.461(4)Å. Bond distances and angles between non-hydrogen O, N and C atoms agree with those reported in aqua- as well as in non-aqua-complexes.[22,26,27] A network of hydrogen bonds [OW-H−O (2.803 to 2.952Å) and N-H−O (3.028Å)] form *inter*-molecular linkages. It may seem from Figure 1 that water molecule OW2 is close enough to the copper atom to be bonded to it, but this is a false impression. OW2 only complete the hydrogen bonding pattern. The copper atom and the OW2 oxygen atom are separated by 3.007Å, somewhat more than the sum of the van der Waals radii for these atoms (1.40 and 1.52Å, respectively).[28]

Upon calculations involving minimisation of conformational energy, the crystal structure converged to a structure with the same conformation for both chelate rings (Table 2). Values of the two most critical torsion angles, Cu-N1-C14-C15 (γ_1) and N1-C14-C15-C16 (γ_2) were better reproduced in ring 2 (difference between theory and experiment equals to 1.2° and 17.0° for the angles γ_1 and γ_2, respectively) than in ring 1 (19.2° and 27.2°). The angles around copper were fairly well reproduced, differences ranging between theory and experiment from 1.30° (O11-Cu-N2) to 6.05° (O11-Cu-O21).

The crystal structure was not equally well reproduced with different force fields (Figs. 2 and 3). Force fields in which interactions with the apically bonded oxygen (denoted with a prime) were also taken into account yielded generally better agreement between theory and experiment both in the reproduction of the shape of the copper coordination polyhedron (expressed as $\varepsilon_{r.m.s.}$ ($\Delta\theta$)) and overall molecular geometry ($\varepsilon_{r.m.s.}$ (Δr)). Force fields with "loose" parameters for angles around

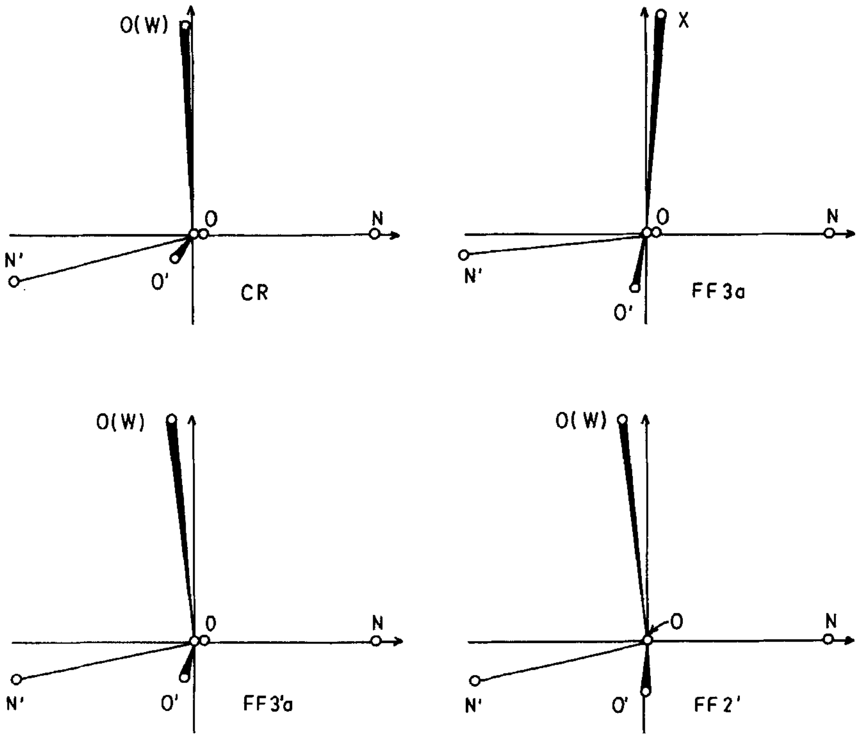

Figure 2 Copper coordination polyhedra obtained by three force fields. X denotes the position of a "dummy" atom, *i.e.*, O(W), without non-bonded interactions with the rest of the molecule. CR denotes crystal structure.

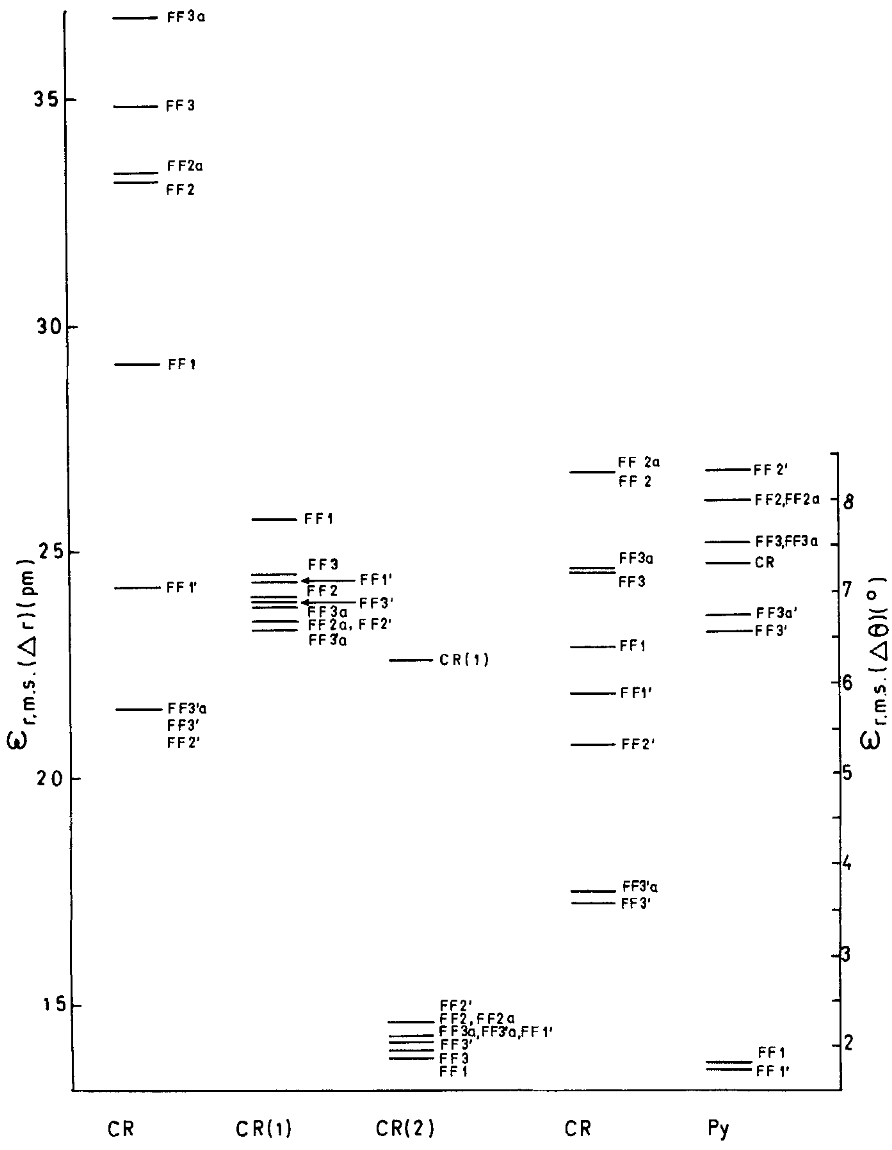

Figure 3 Comparison of X-ray molecular structure (CR) with theoretically predicted conformations (FF1, FF2 etc. denote conformations obtained with respective force fields). Py refers to ideal, undistorted pyramidal configuration; $\varepsilon_{\mathrm{r.m.s.}}(\Delta r)$ values were computed neglecting H atoms; $\varepsilon_{\mathrm{r.m.s.}}(\Delta\theta)$ refers to ten valence angles defining the copper coordination geometry.

copper also better reproduced the crystal structure than the force field FF1 (and FF1') in which "hard" parameters were used. Also, with the latter force fields, structures closer to undistorted coordination polyhedron (Py) were obtained. As should be expected, both chelate rings (CR(1) and CR(2)) were not equally well reproduced in terms of $\varepsilon_{r.m.s.}$ (Δr). Differences in root-mean-square deviations between the two rings are higher than the differences between experimental and theoretical structures of ring 2, and nearly equal to the $\varepsilon_{r.m.s.}$ (Δr) values for ring 1.

From theoretical considerations it can be proposed that aqua*bis*(*L*-*N*-benzylalaninato) copper (II) has altogether 12 possible conformations of chelate rings (six equatorial and six axial conformations), but after systematic searching of conformational space only nine conformations were obtained upon minimisation of strain energy (Table 3). Structures with axial methyl groups and *S* configuration at nitrogen (Me(*a*)*N*(*S*)) were found to be energetically impossible due to steric strain caused by the bulky benzyl group.

By combination of chelate ring conformations, 45 conformers of the *bis*-complex could be proposed, but again substantially less were actually obtained by molecular mechanics calculations (Table 4). The conformer with the lowest energy (9–9 for the *bis*-complex and 2–9 for the aqua-complex) does not correspond to the 1–1 conformer obtained by minimisation of the X-ray structure. On the contrary, crystal conformation (1–1 with the water bound to C^{α}-H side of the molecule) appeared to be a sterically unfavourable structure with a strain energy of 23 kJ mol^{-1} above the global minimum. This fact, together with the observation of unequal distortions of chelate rings in the crystal conformation, strongly suggests a considerable influence of intermolecular interactions in defining the molecular crystal geometry.

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Supplementary Material

Full lists of H atom positions, anisotropic thermal parameters and observed and calculated structure factors are available from N.R. upon request.

Table 3 Minimum conformational energies for the chelate ring of aqua*bis*(*L*-*N*-benzylalaninato) copper(II) monohydrate.*

No.	Ring conformation	γ_1(°)	γ_2(°)	Φ_T(kJ mol^{-1})
1	Me(*e*)*N*(R)	179.27	-79.54	5.90
2		-59.28	-97.13	6.79
3		61.85	-93.13	4.80
4	Me(*e*)*N*(S)	-168.66	45.57	13.56
5		-56.47	94.56	7.75
6		51.61	101.27	12.96
7	Me(*a*)*N*(R)	176.82	-79.24	2.97
8		-59.06	-95.33	0.00
9		59.75	-93.13	1.95

* Calculations were carried out with force field FF3a. Torsion angles γ_1 and γ_2 correspond to angles Cu-N1-C14-C15 and N1-C14-C15-C16, respectively. Zero point: 4.809 kJ mol^{-1}.

Table 4 Relative conformation energies, Φ_T (kJ mol^{-1}), of the conformers of *trans-bis*(*L-N*-benzylalaninato)copper(II) and *trans*-aqua*bis*(*L-N*-benzylalaninato)copper (II).*

Conformer	$(BzAla)_2Cu$	$(BzAla)_2Cu\text{-}H_2O$	
		C^α-H side	C^α-CH_3 side
1 1	23.31	22.92	18.95
1 2	16.46	24.90	12.30
1 3	19.18	22.00	14.66
1 4	28.80	25.06	25.83
1 5	13.30	8.60	
1 6	22.65	18.31	
1 7	17.56	15.33	17.29
1 8	8.81		6.97
1 9	5.88	17.27	5.11
2 2	6.34	28.16	2.29
2 3	7.89	24.05	3.34
2 4	27.03	26.50	23.87
2 5	14.71	12.06	
2 6	21.70	20.51	
2 7	13.72	18.11	13.70
2 9	1.36	20.61	0.00
3 3	10.97	18.68	6.25
3 4	28.84	25.55	24.42
3 5	14.33	9.04	
3 6	18.81	13.52	
3 7	16.44	14.31	16.21
3 8	6.61		4.92
3 9	6.51	14.76	4.97
4 4	33.95	29.69	33.97
4 5	18.52	14.19	
4 6	26.62	22.44	
4 7	22.53	19.22	24.53
4 8	16.00		16.82
4 9	12.92	19.71	15.18
5 7	10.38	9.78	
5 8	2.74		
5 9	0.17		
6 7	20.18	20.78	
6 8	13.11		
6 9	10.00	17.40	
7 7	11.52	9.69	16.11
7 8	2.93		8.10
7 9	1.65		8.62
9 9	0.00	12.10	2.75

*Calculations were carried out with force fields FF3a and FF3'a (for details see Experimental). Zero points: - 5.965 kJ mol^{-1} (FF3a) and - 4.883 kJ mol^{-1} (FF3'a).

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