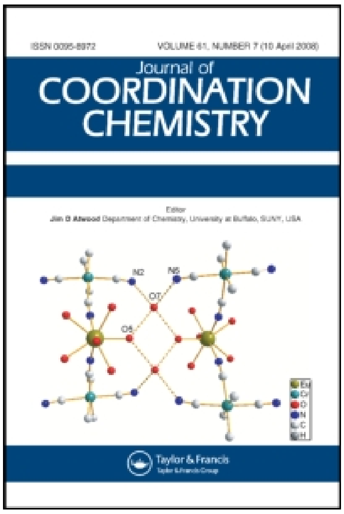

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. XI. CRYSTAL STRUCTURE AND MOLECULAR MECHANICS CALCULATIONS ON RACEMIC AQUABIS(*L-N,N*-DIMETHYLVALINATO)COPPER(II)

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. XI. CRYSTAL STRUCTURE AND MOLECULAR MECHANICS CALCULATIONS ON RACEMIC AQUA*BIS*(*L-N,N*-DIMETHYLVALINATO)COPPER(II)

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(Received May 15, 1985)

The structure of blue, triclinic ($P\bar{1}$) crystals of a 1:1 mixture of *trans*-aqua*bis*(*L-N,N*-dimethylvalinato)copper(II) and its enantiomer was determined by X-ray diffraction methods and refined to R = 0.026. The structure consists of discrete molecules linked with OH–O hydrogen bonds. Coordination around copper(II) is distorted square-pyramidal with valine N and O atoms in the equatorial plane. The O-Cu-OW, O-Cu-N and N-Cu-OW valence angles range from 82.82(7) to 99.11(7)°. Values for O-Cu-O and N-Cu-N are 167.56(8) and 167.59(8)°, respectively. Cu-O [1.932(2), 1.929(2) Å] and Cu-N [2.057(2), 2.043(2) Å] bond lengths have values similar to those in other copper(II) complexes with *N*-alkylated amino acids, but the Cu-OW bond length is very short [2.312(2) Å]. This was attributed to distortion of the coordination polyhedron, and the apical bond length was quite satisfactorily reproduced with a new theoretical method (N. Raos, *J. Mol. Struct.*, in press.). 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 5.2°. The calculated strain energy of the crystal conformation is 9.3 kJ mol^{-1} higher than the energy of the most stable conformer, but it has virtually the same energy as the most stable conformer of the *D, L*-isomer. This points to a very subtle interplay of interactions which determine the structure and conformation of the molecule in the crystal state.

KEYWORDS: *N,N*-dimethylvaline, copper, X-ray structure, conformational analysis, molecular mechanics

INTRODUCTION

There are many reasons for studying copper(II) chelates with *N*-alkylated α-amino acids.[1] The first is to find an explanation for the enantioselectivity effect which has been observed in complexes of *N*-alkylated amino acids[2] but not in chelates of their

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naturally occurring analogues.[3] Also, because of the very pronounced distortion of the coordination polyhedron in the molecules, these complexes are ideal model compounds for development of molecular mechanics methods for the reproduction of "irregular" copper coordination geometry.[4,5]

Copper(II) chelates with α-amino acids and their *N*-alkylated derivatives generally form three kinds of crystal modifications: the *red* modification with square-planar coordination around the central atom, the *blue* modification with the water molecule in one or two apical position(s) and, very rarely, the *green* modification with the cage (acetato-like) structure. The crystal structure of red *bis*(*L-N,N*-dimethylvalinato)copper(II) has already been solved,[6] and recently also the structure of its *D,L*-isomer.[7] Our intention in this paper was to determine the structure of the aqua-complex of this ligand (the blue modification) which fortunately crystallized from an aqueous Cu(II)/*D,L-N,N*-dimethylvaline solution together with the red modification.[7]

At first our interest was focussed on tetracoordinated complexes because of their relative simplicity, essential for the development of molecular mechanics models. However, the finding that there is a variation of apical (Cu-OH_2) bond length, in pentacoordinated copper(II) chelates with *N*-alkylated amino acids,[8] posed a new set of interesting questions. The apical bond length proved to correlate well with various measures for the distortion of the coordination polyhedron from planarity.[9] Also, these findings enabled us to use the functions obtained by regression analysis to estimate the apical bond length from the calculated (by molecular mechanics) geometry of the copper(II) coordination polyhedron.

EXPERIMENTAL

Crystals of the title compound were prepared as described previously.[7] Crystallographic, collection and refinement data are listed in Table 1. The structure was solved by the heavy-atom method.

The position of the copper atom was revealed in a three-dimensional Patterson map. A Fourier synthesis calculated based on the metal atom only provided the positions of all remaining 22 non-H atoms. Hydrogen atoms were found as small positive electron densities in expected positions at reasonable distances from the parent carbon atoms. As the H-atoms were included in the structure factor calculations but not refined, their coordinates were calculated from their expected geometrical positions and orientation [d(C-H) = 0.95 Å]. The hydrogen atoms of water molecules were found in a δF-map calculated at the end of anisotropic refinement and included in the structure factor calculations. Although the compound crystallized from the racemix mixture we established that the copper atom was coordinated by two *L*-isomers. At that point of structure determination the centrosymmetric space group became uncertain and we had to find out whether the same enantiomers were present in the unit cell or not. The correct choice of triclinic space groups was determined by the *MISSYM*[10] program. It was established that the structure implied the inversion centre and the space group $P\bar{1}$ was undoubtedly confirmed. The final difference Fourier map was featureless. Atomic scattering factors for neutral atomic species were taken from *International Tables for X-ray Crystallography.*[11] Programs used for data collection, cell refinement and semi-empirical φ-scan absorption corrections were *DIF4, REDU4* and *EMPIR.*[12-14]

Table 1 Crystal, data collection and structure refinement details.

Empirical formula	$C_{14}H_{28}CuN_2O_6$	Standard reflections (measured every 120 min.)	-1 4 3 -1 -1 5 3 0 3
Colour/habit	blue/blocky		
Size, mm	0.58 × 0.40 × 0.24		
M_r	387.96		
		Intensity variation	±2.5%
Crystal system and space group	triclinic, $P\bar{1}$	Reflections collected:	
Unit cell dimensions[a]		total	4079
a, Å	8.504(3)	independent($R_{int.}$ = 0.021)[b]	3869
b, Å	10.515(3)	Range of h,k,l	-10 to 9, 0 to 13, -14 to 14
c, Å	11.669(4)	Computer programs[c]	DIF4, REDU4, MISSYM, EMPIR, NRCVAX, ORTEPII
α, °	103.96(1)		
β, °	92.95(2)	Transmission factors:	
γ, °	112.79(1)	$t_{min,max}$	0.5788; 0.6833
Cell volume, Å^3	921.2(5)	Final residuals:	
Molecules/cell	2	R	0.026
D_c, g cm^{-3}	1.399	R_w	0.053
μ(MoKα), mm^{-1}	1.21	S	1.59
F(000)	415	Weighting scheme, w	$1/[\sigma^2 F_o + 0.0008F_o^2]$
Diffractometer	PW1100 (Stoe upgraded)	Reflections observed ($I_{net} \geq 2\ \sigma I_{net}$)	3363
		Parameters varied	208
Radiation, λ(MoKα),Å (graphite monochromated)	0.7093	Data-to-parameter ratio	16.2
2θ range,°	4 to 54	$(\Delta/\sigma)_{max}$	0.006
Scan type	ω/2θ	$\delta\rho_{min,max}$, e/Å^{3}	-0.30;0.41

[a] Least squares refinement of position angles of 25 reflections in the range 20 ≤ 2θ ≤33°. [b] Corrections: Lorentz-polarization and semi-empirical ψ-scan absorption corrections. [c]Neutral scattering factors and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Molecular graphics were drawn using *ORTEP*II.[15] Program(s) used for structure solution, refinement and preparing the material for publication were contained in the *NRCVAX*[16] suite of programs.

Conformational analysis

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

$$V_T = \frac{1}{2}\sum_i k_{b,i}(b_i - b_{o,i})^2 + \frac{1}{2}\sum_j k_{\theta,j}(\theta_j - \theta_{o,j})^2 + \frac{1}{2}\sum_k V_{n,k}(1 \pm \cos n_k \phi_k) + \sum_l [A_l \exp(-B_l r_l) - C_l r_l^{-6}] + \frac{1}{2}\sum_m k_{x,m}\chi_m^2 \qquad (1)$$

where b, θ, ø and χ stand for bond lengths, valence, torsion and out-of-plane angles, respectively; r is a non-bonded distance. k_b is an empirical parameter for bond stretching and k_θ for valence angle bending; b_o and θ_o are equilibrium bond and valence angle values, respectively. Torsion interactions were determined with parameters V_n and n (height and multiplicity of torsional barrier, respectively) and non-bonded interactions were computed from Buckingham functions with parameters A, B and C. In addition, the out-of-plane deformation potential (k_χ = 100 kcal mol^{-1} rad^{-2}) for the angle defined with four atoms in the carboxyl group was calculated for the force fields marked with an *a*.*

The force fields (FF2', FF3'a, *etc.*) used in this paper were as defined elsewhere.[9,17,18] Computations were done with the CFF program[19] for conformational analysis.

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

$$rms = \left[\frac{1}{N}\sum_{i=1}^{N}(\Delta X_i)^2\right]^{1/2} \qquad (2)$$

where X stands for either valence angles (θ) around copper or interatomic distances (r) among all non-hydrogen atoms. Δ denotes the difference between values of observable X in two structures.

RESULTS AND DISCUSSION

An *ORTEP*II perspective view of the molecule in a general orientation with the hydrogen bonding pattern is shown in Figure 1. The superimposition of two *L,L* molecules of the aqua complex and of the previously determined *bis*(*L-N,N*-dimethylvalinato)copper(II)[6] anhydrous complex showing significant conformational differences is displayed in Figure 2. Table 2 summarizes final atomic

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* Here, 1 cal = 4.184 J.

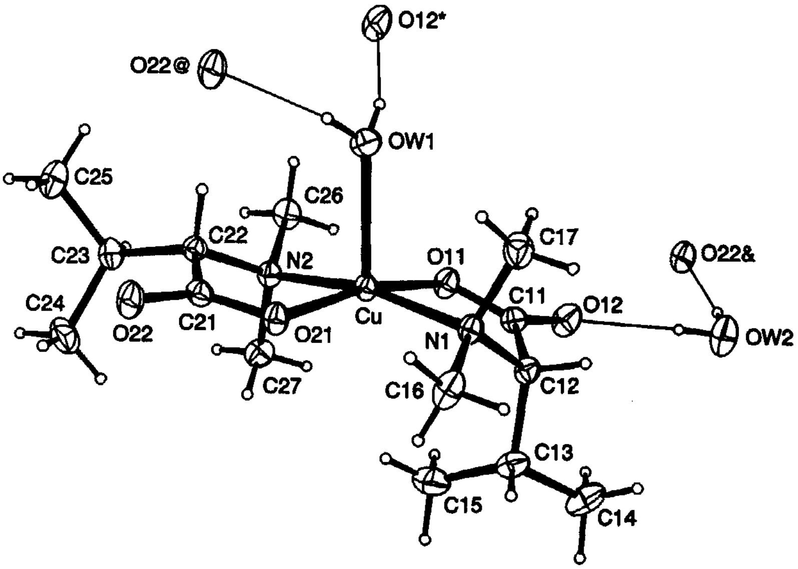

Figure 1 An *ORTEP*II view of an *L,L* molecule of aqua*bis*(*L-N,N*-dimethylvalinato)copper(II) showing the numbering scheme. Intermolecular hydrogen bonds are indicated by thin lines. Non-hydrogen atoms are shown with displacement ellipsoids at the 30% probability level. For clarity, the H atoms are drawn as small spheres of arbitrary size. Symmetry code: (@) −x, −y, 1 − z; (*) −x, −y, −z; (&) x, y, −1 + z.

coordinates and parameters for isotropic equivalent thermal displacement and Table 3 lists experimental and theoretical values of bond lengths, valence angles and selected torsion angles for non-hydrogen atoms.

Racemic aqua*bis(N,N*-dimethylvalinato)copper(II) crystallizes with water of crystallization. The copper atom coordination environment is an irregular square pyramid with N and O valinato ligand atoms in the equatorial plane *trans* to each other [*d*(Cu-O) = 1.932(2) and 1.929(2) Å, *d*(Cu-N) = 2.057(2) and 2.043(2) Å] and an apically positioned coordinated water molecule [*d*(Cu-OW1) = 2.312(2) Å]. This distance is within the range of typical apical bond lengths (2.206 to 2.464 Å) observed in similar structures[9] (for detailed discussion see below). There is no significant difference in Cu-O and Cu-N bond distances with respect to this structure and similar amino acid copper complexes.[1,6-8,20-23]

The copper atom is situated 0.21 Å above the O11, O21, N1, N2 equatorial plane, towards OW1. There is good agreement of O-Cu-N angles with corresponding values found in the anhydrous *L,L*[6] and *D,L*[7] analogues and discrepancies for O-Cu-O and N-Cu-N angles. Angles involving the metal atom, donor atoms and coordinated water are in the range 93.21(7) to 99.11(7) Å. The conformation of both chelate rings is in the form of an open envelope with N1 and N2 displaced from the planes defined by Cu, O11, C11, C12 and Cu, O21, C21, C22 by 0.58 and 0.62 Å, respectively. All O-C, N-C and C-C bond lengths are normal.[24] The crystal structure is dominated by intermolecular OW-H---O hydrogen bonds ranging from 2.802(3) to 2.927(3) Å.

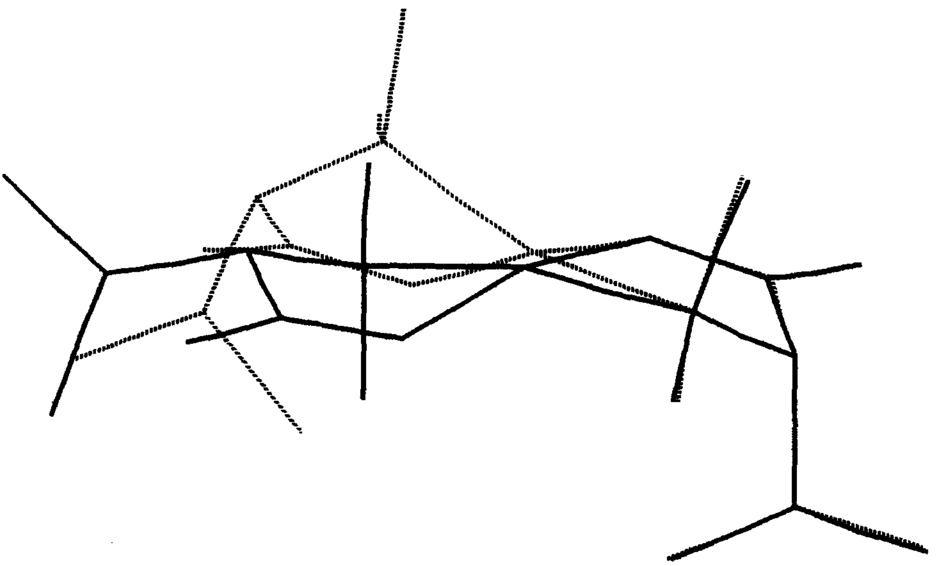

Figure 2 Visual comparison of molecules of the anhydrous (dotted lines)[6] and aqueous (solid lines) forms of bis(*L*-*N*,*N*-dimethylvalinato)copper(II), showing the difference in conformation of the left chelate ring. O11, N1, C11 and C12 atoms in both cases were used for molecular least-squares fitting. The coordinated water molecule, water of crystallization of aqueous complex and all hydrogen atoms are omitted for clarity.

Reproduction of the crystal structure by means of the molecular mechanics method demonstrated that different coordination polyhedra were obtained upon minimization of the initial structure (Fig. 3). The coordination geometry defined by four atoms from chelate rings and copper can be described in all theoretical structures as a very flattened tetrahedron. On the contrary, in the crystal structure it is essentially a square pyramid. Disagreement of this kind is seldom found in aqua-complexes of *N*-alkylated amino acids,[21] or in their anhydrous complexes[6,18] and very probably can be attributed to imperfections in the molecular mechanics model.[25]

All force fields reproduce the apical bond length close to their b_0 parameter value (2.475 Å for FF2' and FF3'a, 2.352 Å for other force fields). From the functions derived by multiple linear regression for crystal structures of aqua-copper(II) complexes of *N*-alkylated amino acids,[9] the Cu-OW1 bond length can be calculated. Results are 2.324 and 2.325 Å from regressions within the frame of *trans* (N-Cu-N and O-Cu-O) angles and from the function of N-Cu-N and the sum of the *cis* angles, respectively. This is in accordance with the measured value of 2.312(2) Å. Due to the poor theoretical reproduction of copper coordination geometry, the values of Cu-OW1 bond length range from 2.415 to 2.336 Å (the first regression function) and from 2.460 to 2.447 Å (the second regression function) for all six force fields. The best agreement with experimental values was obtained with the force field FF6'a by using the multiple regression function of *trans* angles (2.336 Å). This is in agreement with the conclusion, based on the results of analysis of seven

Table 2 Final atomic fractional coordinates (× 10^4; × 10^5 for Cu) and equivalent isotropic thermal displacement coefficients B_{eq}(Å^2).

	x/a	*y/b*	*z/c*	B_{eq}*
Cu	22368(3)	9650(3)	24361(2)	1.98(2)
O11	2287(2)	652(2)	740(1)	2.7(1)
O12	3253(3)	1730(2)	-645(1)	3.6(1)
N1	3134(2)	3085(2)	2438(2)	2.2(1)
C11	3139(3)	1762(3)	406(2)	2.4(1)
C12	4094(3)	3193(2)	1392(2)	2.3(1)
C13	6019(3)	3540(3)	1668(2)	3.0(1)
C14	6921(4)	4043(3)	658(3)	4.2(1)
C15	6376(4)	2310(4)	1901(3)	4.9(2)
C16	4168(4)	4104(3)	3596(2)	3.3(1)
C17	1626(4)	3413(3)	2188(3)	3.5(1)
O21	2692(2)	1306(2)	4145(1)	2.5(1)
O22	2150(2)	261(2)	5594(1)	3.2(1)
N2	1888(2)	-1076(2)	2413(2)	2.1(1)
C21	2115(3)	203(2)	4523(2)	2.2(1)
C22	1250(3)	-1264(2)	3562(2)	2.0(1)
C23	1275(3)	-2587(2)	3909(2)	2.7(1)
C24	2917(4)	-2348(4)	4688(3)	4.1(2)
C25	-318(4)	-3232(3)	4487(3)	3.9(1)
C26	637(3)	-2176(3)	1363(2)	3.0(1)
C27	3590(3)	-1130(3)	2350(2)	2.9(1)
OW1	-655(2)	497(2)	2424(1)	2.9(1)
OW2	3862(3)	3026(2)	-2567(2)	4.4(1)

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

molecules, that the force field FF6'a and the latter regression generally gives the best results.[9]

Comparison of structures (overall geometry and angles around copper) revealed that the crystal structure reproduced reasonably well with all force fields (Fig. 4). Both chelate rings were not equally well reproduced. The first ring [CR(1), conformation 6 according to our notation[26]] was more poorly reproduced than ring 2 [CR(2), conformation 1], but the difference, expressed as *rms*(Δr), was not larger than the difference between crystal structures with the same conformation (LL(1), LL(2), DL).[6,7] The difference between the first chelate ring of the aqua-complex and the rings in crystal structures of other copper(II), *N,N*-dimethylvalinates was smaller than the difference between two rings [LL(1) and LL(2)] of the same conformation in the crystal structure of *bis*(*L*-*N,N*-dimethylvalinato)copper(II)[6] (*rms*(Δr) = 7.4 pm).

Comparison of *rms*($\Delta\theta$) values reveals that all force fields reproduce the coordination polyhedron equally, with the exception of FF2' and FF6'a. The reason for this small discrepancy is that force field FF2' has very strong parameters for the valence-angle bending potential which holds the atoms in the chelate plane, and FF6'a was not in fact parametrized to yield the best *rms*($\Delta\theta$) value but to obtain the best fit with the experimental N-Cu-N angle.[9] Calculation of *rms*($\Delta\theta$) with respect to the ideal pyramid showed that the crystal structure was much more distorted from planarity than theoretical structures. Again, the proximity of the structure obtained with FF2' to the undistorted coordination polyhedron can be easily attributed to too strong parameters for valence-angle bending potentials for copper interactions.

Table 3 Interatomic distances (Å), valence angles (°) and selected torsion angles (°).

Internal coordinate	Experimental value	Theoretical value (FF3'a)
Cu-O11	1.932(2)	1.962
Cu-N1	2.057(2)	2.018
Cu-O21	1.929(2)	1.955
Cu-N2	2.043(2)	2.015
Cu-OW1	2.312(2)	2.479
O11-C11	1.277(3)	1.284
O12-C11	1.229(3)	1.241
N1-C12	1.506(3)	1.487
N1-C16	1.482(3)	1.484
N1-C17	1.483(3)	1.483
C11-C12	1.538(3)	1.521
C12-C13	1.531(3)	1.563
C13-C14	1.528(4)	1.549
C13-C15	1.518(4)	1.550
O21-C21	1.268(3)	1.280
O22-C21	1.235(3)	1.240
N2-C22	1.500(3)	1.488
N2-C26	1.483(3)	1.483
N2-C27	1.475(3)	1.479
C21-C22	1.543(3)	1.524
C22-C23	1.548(3)	1.568
C23-C24	1.525(4)	1.555
C23-C25	1.534(4)	1.550
O11-Cu-N11	82.82(7)	84.54
O11-Cu-O21	167.56(8)	172.90
O11-Cu-N2	94.53(7)	98.19
O11-Cu-OW1	99.11(7)	87.44
N1-Cu-O21	97.13(7)	92.78
N1-Cu-N2	167.59(8)	170.39
N1-Cu-OW1	98.39(7)	98.72
O21-Cu-N2	82.85(7)	85.55
O21-Cu-OW1	93.21(7)	86.47
N2-Cu-OW1	94.00(7)	90.63
Cu-O11-C11	116.2(1)	111.9
Cu-N1-C12	105.7(1)	106.3
Cu-N1-C16	113.3(2)	112.5
Cu-N1-C17	108.4(2)	106.3
C12-N1-C16	114.1(2)	113.4
C12-N1-C17	107.3(2)	109.6
C16-N1-C17	107.8(2)	108.5
O11-C11-O12	123.4(2)	119.6
O11-C11-C12	117.2(2)	118.9
O12-C11-C12	119.4(2)	121.5
N1-C12-C11	106.7(2)	105.8
N1-C12-C13	115.3(2)	114.8
C11-C12-C13	111.2(2)	109.2
C12-C13-C14	109.3(2)	110.2
C12-C13-C15	113.8(2)	112.7
C14-C13-C15	111.3(3)	108.8
Cu-O21-C21	116.1(1)	112.2
Cu-N2-C22	104.9(1)	104.9
Cu-N2-C26	112.3(1)	110.0
Cu-N2-C27	106.4(1)	105.3
C22-N2-C26	111.3(2)	111.7
C22-N2-C27	112.9(2)	114.3
C26-N2-C27	108.9(2)	110.4

Table 3 — Continued

O21-C21-O22	123.6(2)	117.9
O21-C21-C22	116.4(2)	118.3
O22-C21-C22	120.0(2)	123.7
N2-C22-C21	108.0(2)	108.2
N2-C22-C23	115.4(2)	114.8
C21-C22-C23	117.0(2)	115.2
C22-C23-C24	116.4(2)	114.6
C22-C23-C25	109.3(2)	109.5
C24-C23-C25	110.7(2)	107.8
N1-Cu-O11-C11	14.7(1)	6.8
N2-Cu-O21-C21	-20.2(1)	-9.5
O11-C11-C12-N1	-26.5(1)	-34.9
N1-C12-C13-C14	-163.7(2)	-174.7
O21-C21-C22-N2	21.4(1)	30.5
O11-Cu-N1-C16	-153.3(1)	-149.8
O21-Cu-N2-C26	150.6(1)	145.0
Cu-O11-C11-C12	3.1(1)	14.3
Cu-N1-C12-C13	-89.8(1)	-84.9
Cu-O21-C21-C22	4.3(1)	-9.3
Cu-N2-C22-C23	-166.6(2)	-163.9
N2-C22-C23-C25	-142.9(2)	-150.8

From the fact that the *N,N*-dimethylvalinato chelate ring has six conformations (three with the equatorial position of the isoprolyl group, 1...3, and the same number of conformations with the group in the apical position, 4...6)[26] and that the

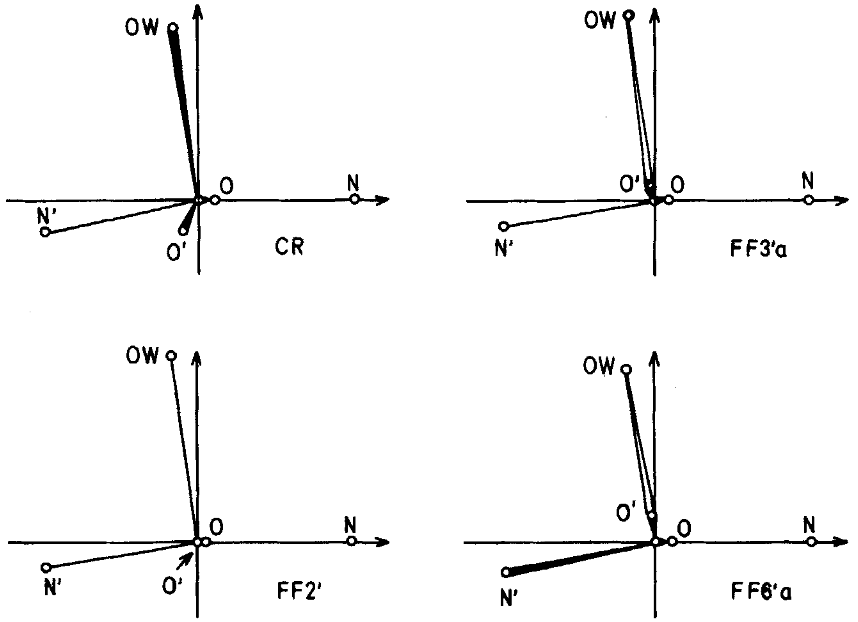

Figure 3 Copper coordination polyhedra obtained by three force fields. CR denotes the crystal structure.

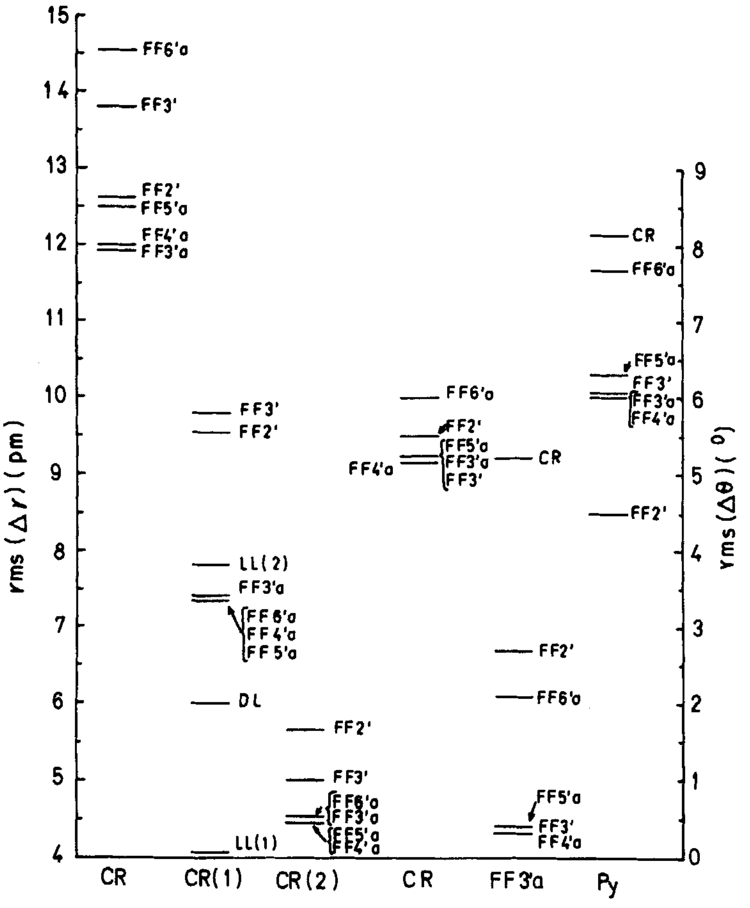

Figure 4 Comparison of X-ray (CR) with theoretically predicted conformations (FF2', FF3'a *etc.*). CR(1) denotes the crystal structure of the right and CR(2) the structure of left ring (see Figs. 1 and 2). Py refers to ideal, undistorted pyramidal conformation; *rms*(Δ*r*) values were computed neglecting H atoms; *rms*(Δθ) refers to ten valence angles defining the copper coordination geometry.

water molecule can be bonded to both sides of the molecule, total of 42 conformations of *trans*-aqua*bis*(*L*-*N*,*N*-dimethylvalinato)copper(II) can be proposed (Table 4). The conformer observed in the crystal structure (6–1 LL, C^{α}-H) did not have the lowest conformational energy. On the contrary, its energy was 9.31 kJ mol^{-1} above the global minimum (6–6 LL, C^{α}-H). The rest of the conformers (with the exception of conformer 4–6 LL, C^{α}-H) had higher energy, up to 56.28 kJ mol^{-1} above the global minimum (5–5 LL, C^{α}-R). Conformers with the water molecule placed on the C^{α}-R (*i.e.*, isopropyl) side of the molecule generally had higher energy; this was obviously due to the closer contact of the bulky isopropyl group and the water molecule. All high-energy conformers had very distorted calculated coordination polyhedra and it is highly doubtful that they actually reproduced the molecular geometry and energy.

Table 4 Relative conformational energy (kJ mol^{-1}) of the conformers of two diastereomers of *trans*-aqua*bis(N,N*-dimethylvalinato)copper(II).*

Conformer		*L,L-isomer*		*D,L*-isomer	
		C$^{\alpha}$-H side	C$^{\alpha}$-R side	C$^{\alpha}$-H side	C$^{\alpha}$-R side
1	1	25.55	27.33	17.05	(same)
1	2	33.66	33.73	24.63	24.05
1	3	27.55	27.01	18.74	17.64
1	4	20.33	26.58	10.54	14.79
1	5	24.99	38.71	16.58	25.95
1	6	9.31	24.76	0.57	12.26
2	2	42.18	40.46	31.95	(same)
2	3	36.30	33.58	26.15	25.29
2	4	27.89	33.00	14.02	22.68
2	5	33.51	45.05	23.34	33.45
2	6	17.68	31.07	7.48	19.78
3	3	29.40	26.38	19.23	(same)
3	4	22.11	26.42	10.21	16.40
3	5	25.75	38.64	15.85	27.75
3	6	10.51	24.40	0.00	14.07
4	4	13.20	25.41	10.37	(same)
4	5	21.50	38.92	18.14	24.56
4	6	5.59	25.23	2.43	10.99
5	5	33.07	56.28	36.18	(same)
5	6	16.48	42.28	19.88	19.52
6	6	0.00	27.56	3.52	(same)

*Calculations were performed with force field FF3'a (for details see Experimental). Zero point energies: 30.246 kJ mol^{-1} (*L,L*-isomer), 40.197 kJ mol^{-1} (*D,L*-isomer). Side in *D,L*-isomer refers to the side with respect of the first chelate ring.

The fact that from the racemic mixture crystallized aqua*bis*(*L-N,N*-dimethylvalinato)copper(II) and its enantiomer and not its diastereomer, aqua*bis*(*D,L-N,N*-dimethylvalinato)copper(II), led us to a conformational analysis of the *D,L*-isomer (Table 4). The lowest conformer of a *D,L*-isomer (3–6 DL, C$^{\alpha}$-H) has an energy 9.95 kJ mol^{-1} higher than the global minimum of the *L,L*-isomer, but virtually the same energy as the conformer observed in the crystal state. Therefore it can be concluded that the conformation of the molecule in the crystal state is determined by a very subtle interplay of sterical intramolecular forces and packing interactions determined mainly by hydrogen bonding.

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SUPPLEMENTARY MATERIAL

A full list of H atom positions, anisotropic thermal parameters and observed and calculated structure factors is available from N. R. upon request.

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