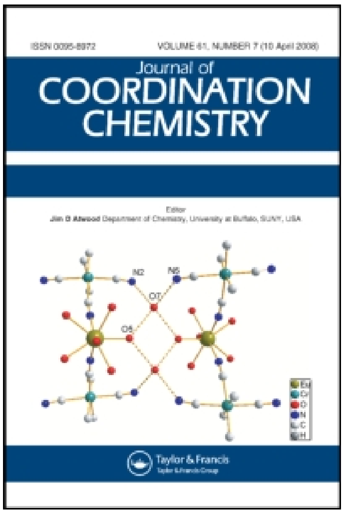

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Stereochemistry of complexes with *n*-alkylated amino acids. xii. crystal structure and molecular mechanics calculations for aqu a*bis*(*l*-*n, n*-dimethylalaninato)copper(ii) hexahydrate

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. XII. CRYSTAL STRUCTURE AND MOLECULAR MECHANICS CALCULATIONS FOR AQUA*BIS(L-N,N*-DIMETHYLALANINATO)COPPER(II) HEXAHYDRATE

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The structure of blue, monoclinic (*C*2) crystals of *trans*-aqua*bis(L-N,N*-dimethylalaninato-)copper(II) hexahydrate was determined by X-ray diffraction methods and refined to $R = 0.026$. The structure consists of discrete molecules in the same (*equatorial-equatorial*) conformation linked together in a comprehensive array of water molecules with the structure resembling that of ice. The copper coordination polyhedron is highly distorted [N-Cu-N′ = 166.2(1)° and O-Cu-O′ = 161.5(1)°] and the apical bond length [Cu-OW = 2.222(3) Å] is extremely short, which is a direct consequence of the distortion of the coordination polyhedron. Conformational analysis shows that the conformation of the molecule in the crystal state is 1.4 kJ mol^{-1} higher in energy than the most stable conformer (with *axial-axial* conformation).

Keywords: copper; amino acids; X-ray structure; energetics

INTRODUCTION

Copper(II) chelates with *N*-alkylated and *N,N*-dialkylated α-amino acids [1] are a class of compounds which has been systematically studied by our group for more than a decade. These compounds have, due to close contact of bulky

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substituents on nitrogen atoms, very pronounced distortion of the coordination polyhedron, which led us to develop a number of molecular mechanics models for the simulation of the shape of both tetracoordinated [2-4] and pentacoordinated (*aqua*) complexes. [5]

Analysis of the shape of the pentacoordinated copper(II) chelates with *N*-alkylated amino acids revealed that the Cu-OH_2 appical bond length correlated with the distortion of coordination polyhedron from planarity, and was mainly dependent on the N-Cu-N′ *trans* angle. [5] Further analysis showed that there are two kinds of (distorted) coordination polyhedra in this class of compounds: group I compounds (N-Cu-N′ > O-Cu-O) are distorted "square pyramids", and group II compounds (N-Cu-N′ < O-Cu-O′) are distorted "trigonal bipyramids". [6] Interestingly, group I consists exclusively of *N,N*-dimethylated derivatives.

The aim of this paper is first to answer to three specific questions: (1) is the conformation of the compound observed in the crystal state the most stable conformation; (2) are the molecular mechanics models capable of reproducing geometry of the molecule as observed in the crystal state; (3) is the shape of the coordination polyhedron a direct consequence of the molecular structure, *i.e.*, is it necessary for *N,N*-dimethylated derivatives to belong to the group I of distorted coordination polyhedra. Answers to these questions would throw more light not only to this particular class of compounds, but other copper compounds as well.

EXPERIMENTAL

The ligand, *L-N,N*-dimethylalanine was prepared by the modified method of Bowman and Stroud, [7] *i.e.*, by condensation with formaldehyde, followed by catalytic hydrogenation in ethanol-water (1:1) solution. The product was recrystallized three times from water/ether, total yield 50%, m. p. 181-2°C. Its structure was confirmed by C,H,N analysis and NMR spectroscopy. The copper complex was prepared by the reaction of the ligand and copper(II) acetate monohydrate in dry CH_2Cl_2. [8] Crystals suitable for X-ray analysis were prepared from water/acetone solution by slow evaporation.

Crystal Structure Determination

Crystallographic, cell constant, collection and refinement data are listed in Table I. The structure was solved applying heavy-atom method. Using the copper atom contribution to the structure amplitudes the positions of all remaining non-H atoms were found in a δF map. Refinement was carried out by full-matrix least-square methods based on *F*. The hydrogen atoms were generated in

TABLE I General and crystal data and summary of intensity data collection and structure refinement.

mpirical formula	$C_{10}H_{34}CuN_2O_{11}$	Standard reflections	−205; 800; 042; 116
olour/habit	blue/prism	(measured every 90 min.)	
ize, mm	0.47 × 0.40 × 0.21	Intensity variation	±2.4%
$_r$	421.93	Friedel pairs collected:	
rystal system, space group	monoclinic, $C2$	total	2387
nit cell dimensions[a]		independent ($R_{int.}$ = 0.024)[b]	2228
, Å	12.300(1)	Unique set h, k, l range	−15 to 14, 0 to 10, 0 to 13
, Å	8.018(2)	Computer programs[c]	STAD14, X-RED, NRCVAX
, Å	10.795(3)		DIFABS, ORTEPII, PLUTON92
, °	107.51(2)	Absorption factors range	min. 0.814 to max. 1.222
ell volume, Å^3	1015.2(4)	Final residuals:	
olecules/cell, Z	2	R	0.026
$_c$, g cm^{-3}	1.38	R_w	0.035
(Mo$K\alpha$), mm^{-1}	1.11	S	1.03
(000)	450	Weighting scheme, w	$1/[\sigma^2 F_o + 0.0008 F_o^2]$
iffractometer	PW1100	Reflections observed	
Stoe upgraded)		($I_{net} \geq 2\sigma(I_{net})$)	2198
adiation, λ(MoKa), Å	0.71069	Parameters varied	110
graphite monochromated)		Data-to-parameter ratio	20
Θrange,°	4 to 54	$(\Delta/\sigma)_{\max}$	0.002
can type	ω	$\Delta\rho_{\min,\max}$, e/Å^3	−0.57; 0.29

[a] Least squares refinement of position angles of 22 reflections in the range 20 ≤ 2Θ ≤ 32°. [b] Corrections: Lorentz-polarization and empirical absorpt orrections based on the best isotropic model. [c] Neutral scattering factors and anomalous dispersion corrections from *International Tables for X-* *rystallography* (1974).

geometrical positions at $d(\text{C-H}) = 0.95$ Å, whereas those belonging to the water molecules were found as small positive electron density maxima in an electron density map at the end of anisotropic refinement. The correct spatial orientation of the methyl groups was verified by electron-density contour drawings calculated through the methyl hydrogen atoms. The complex crystallizes in the monoclinic space group $C2$ with the copper atom and water molecule on the two-fold axis. The polar axis direction has been properly determined by refining Rogers' chirality parameter. Empirical absorption correlations were performed based on the best isotropic model (the min. and max. absorption coefficients were 0.814 and 1.222, respectively). Programs used for data collection, cell refinement and empirical absorption corrections were STADI4, X-RED and DIFABS. [9-11] Molecular graphics used were ORTEPII, PLUTON92. [12, 13] Programs used for structure solution, refinement and preparing the publishing material were contained in the NRCVAX suite of programs. [14]

Conformational Analysis

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

$$\begin{aligned} V_{\mathrm{T}} = {} & \frac{1}{2} \Sigma\, k_{\mathrm{b,i}}(b_{\mathrm{i}} - b_{\mathrm{o,i}})^2 + \frac{1}{2} \Sigma\, k_{\theta,\mathrm{j}}(\theta_{\mathrm{j}} - \theta_{\mathrm{o,j}})^2 \\ & + \frac{1}{2} \Sigma\, V_{\mathrm{n,k}}\,(1 \pm \cos n_{\mathrm{k}}\phi_{\mathrm{k}}) + \sum_{\mathrm{l}} [A_{\mathrm{l}} \exp(-Br_{\mathrm{l}}) - C_{\mathrm{l}} r_{\mathrm{l}}^{-6}] \\ & + \frac{1}{2} \sum_{k} {}_{\chi,\mathrm{m}}\, \chi_{\mathrm{m}}^2 \end{aligned} \tag{1}$$

where b, θ, ϕ and χ stand for bondlengths, 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 ($k_\chi = 100$ kcal mol^{-1} rad^{-2}) for the angle defined with four atoms in the carboxyl group was also calculated (1 cal = 4.184J).

The force fields (FF3'a, FF6'a *etc.*) used in this paper were defined elsewhere. [5, 15] Computations were done with the CFF program [16] for conformational analysis.

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

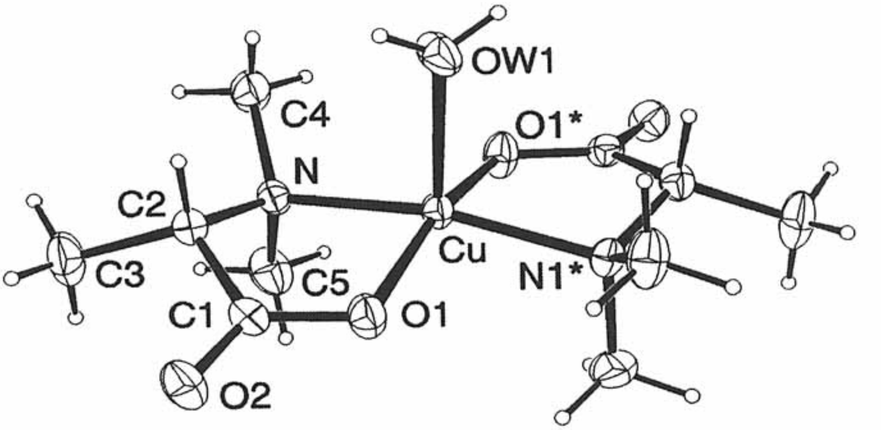

FIGURE 1 Perspective view of the molecule showing the crystallographic numbering scheme. The vibrational ellipsoids are drawn at the 30% probability level. Hydrogen atoms are drawn as small spheres of arbitrary size. Symmetry code: (*) $-x, y, -z$.

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

where X usually stands for ten valence angles around copper (rms^{Py}). Δ denotes the difference between values of observable X in two structures.

RESULTS AND DISCUSSION

A molecule of aqua*bis(L-N,N*-dimethylalaninato)copper(II) hexahydrate in a general orientation with our crystallographic numbering scheme is depicted in Fig 1. The unit cell contents (Table II) with existing hydrogen bond patterns suggest the presence of a comprehensive three-dimensional array (Fig 2). The complex crystallizes as a hydrate with six water molecules of crystallization, which are bonded to carboxylic groups and to the water molecule lying on the two-fold axis. So far, two crystal structures of copper aminoacidates with bidentate *L*-alaninato ligands have been determined, the anhydrous red and the aqua blue modification both being *N,N*-diethyl derivatives. [17, 18]

The copper atom coordination environment is an irregular square-pyramid [O1-Cu-OW1 = 99.3(1)° and N1-Cu-OW1 = 96.9(1)°] with N and O alaninato donor atoms in the equatorial plane *trans* to each other [Cu-O1 = 1.942(1) Å and Cu-N = 2.028(2) Å] and a water molecule in the apical position [Cu-OW1 =

TABLE II Final atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal displacement coefficients B_{eq} (Å^2).

x/a		*y/b*	*z/c*	B_{eq}*
Cu	0	0	0	2.36(1)
O1	1117(1)	−390(2)	−913(1)	3.46(8)
O2	2949(1)	−587(2)	−662(2)	3.68(7)
N	1348(1)	−305(2)	1616(2)	2.61(7)
C1	2154(2)	−349(2)	−215(2)	2.6(7)
C2	2374(1)	129(4)	1217(2)	2.79(7)
C3	3504(2)	−543(4)	2100(2)	4.9(1)
C4	1332(2)	−2092(4)	1972(3)	4.3(1)
C5	1270(2)	738(4)	2717(2)	4.2(1)
OW1	0	2771(3)	0	4.1(1)
OW2	5000	2275(4)	5000	4.9(1)
OW3	0	1986(4)	5000	4.4(1)
OW4	1315(2)	4637(2)	4275(2)	4.72(9)
OW5	3344(2)	4586(2)	3560(2)	4.42(8)

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

2.222(3) Å]. The Cu-O1 bond length is one of the longest and the same as in the *N,N*-dimethylisoleucinato copper complex (1.949(5) Å), [19] while the Cu-N bond distance belongs to the shortest kind (2.010(2) Å). [20] The copper atom displacement out of the basal plane defined by donor atoms O1, N and their symmetry related logeners is remarkable, amounting to 0.278 Å. In previously determined crystal structures of numerous copper *aqua*-aminoacidates with various *N*-substituents, the metal-to-water bond length was established to be in the range from 2.206(3) Å in aqua*bis(L-N,N*-dimethylthreoninato)copper(II) dihydrate, [21] to a maximum of 2.464(2) Å in aqua*bis(N-tert*-butyl-*N*-methylglycinato)copper(II). [22]

The O1-Cu-O1^{i} [161.5(1)°] and N-Cu-N^{i} [166.2(1)°] valence bond angles deviate significantly from linearity. Molecules of the aqua complex generate infinite chains through the strong O2---OW1^{ii} = 2.743(2) Å hydrogen bond along the *x* axis. Six waters of crystallization are inverwoven mutually by hydrogen bridges, connecting the parallel chains with the same interactions forming an endless three-dimensional network clearly visible in Fig 2. OW---OW hydrogen bond distances range from 2.825(3) to 2.917(3) Å, while OW---O bond between the aqua complex in its infinite chains and water molecules are of the three-centred type, *i.e.*, O1---OW5^{iii} = 3.122(3) and O2---OW5^{iii} = 3.057(2) Å. The bondlengths in the bindentate *N,N*-dimethylalaninato ligand are comparable to values reported elsewhere. [23]

Comparison of experimentally obtained and theoretical values (obtained by molecular mechanics calculations) for internal coordinates (Table III) revealed that bond lengths were reproduced with *rms* = 0.015 Å, bond angles with *rms* = 2.0°, close to values obtained for similar molecules. [19-22] Exceptions are the angles around copper which were reproduced with rms^{Py} = 5.6° (FF3'a). Other force fields yielded similar results (rms^{Py} = 6.1° for FF4'a, 5.9° for FF5'a and 5.4° for FF6'a), which was in some degree worse than the results obtained with the respective force fields for other *N*-alkylated aminoacidates (rms^{Py} = 3.06 – 6.1°; mean 4.65°). [5] This result suggests that the shape of the coordination sphere was also determined by the extensive hydrogen bonding in the crystal lattice.

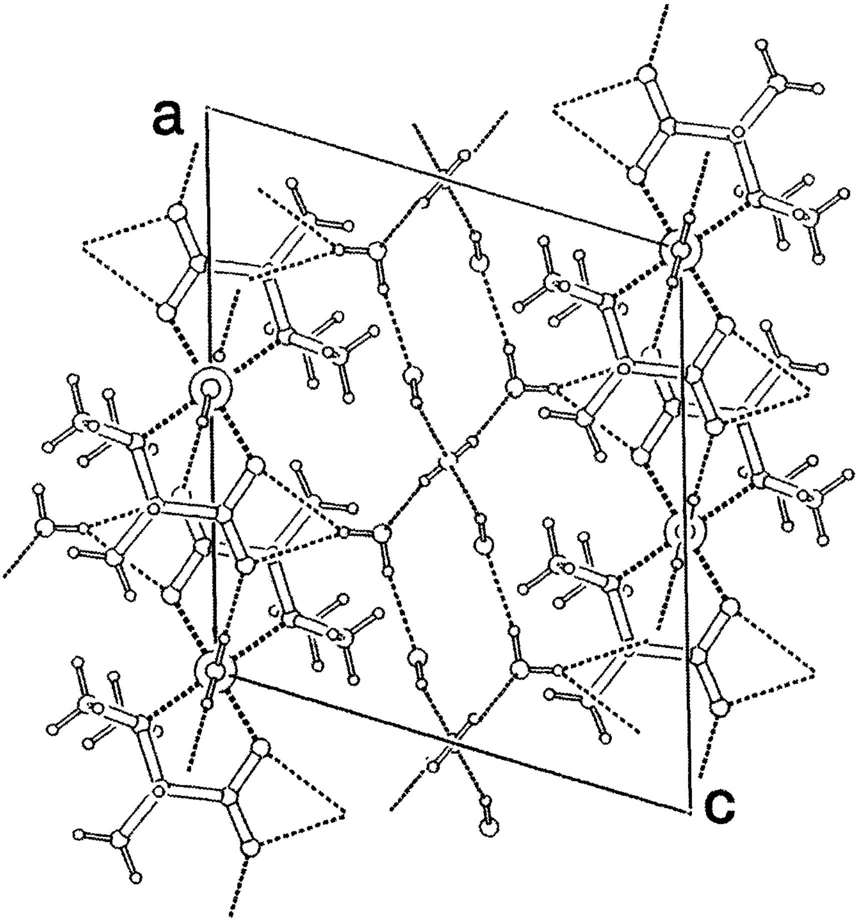

FIGURE 2 Diagram of the unit cell contents in the *ac* projection showing the three-dimensional hydrogen bond pattern between the complex and the water molecules.

TABLE III Interatomic distances (Å), valence angles (°) and selected torsion angles (°).[a]

Internal coordinate	*Experimental value*	*Theoretical value (FF3'a)*
Cu-OW1	2.222(3)	2.476 (2.354)[#]
Cu-O1	1.942(1)	1.959
Cu-N	2.028(2)	2.013
C1-O1	1.272(2)	1.279
C1-O2	1.229(2)	1.241
N-C2	1.492(2)	1.484
N-C4	1.485(3)	1.481
N-C5	1.480(3)	1.482
C1-C2	1.536(3)	1.517
C2-C3	1.528(3)	1.552
O1-Cu-OW1	99.3(1)	92.2
N-Cu-OW1	96.9(1)	95.5
O1-Cu-N	84.1(1)	85.8
O1-Cu-N*	93.7(1)	93.8
O1-Cu-O1*	161.5(1)	175.6
N-Cu-N*	166.2(1)	168.9
Cu-O1-C1	115.6(1)	111.4
Cu-N-C2	105.5(1)	104.1
Cu-N-C4	105.5(1)	105.4
Cu-N-C5	112.9(1)	111.5
C2-N-C4	112.2(2)	110.8
C2-N-C5	111.4(2)	113.1
C4-N-C5	109.2(2)	110.8
O1-C1-O2	122.6(2)	119.4
O1-C1-C2	116.4(2)	118.2
O2-C1-C2	120.9(2)	122.4
N-C2-C1	108.9(2)	108.0
N-C2-C3	115.3(2)	113.7
O1-Cu-N-C4	−94.2(1)	−94.1
Cu-N-C2-C3	−160.3(2)	−160.9
O1-C1-C2-N	25.7(1)	34.9
Cu-O1-C1-C2	−4.4(1)	−13.1
N-Cu-O1-C1	−12.2(1)	−7.7
O1---OW5^{i}	3.122(3)	
O2---OW1^{ii}	2.743(2)	
O2---OW5^{i}	3.057(2)	
OW2---OW4^{ii}	2.910(3)	
OW2---OW5	2.845(3)	
OW3---OW4	2.917(3)	
OW3---OW5^{iii}	2.892(3)	
OW4---OW5	2.825(3)	

[a] Symmetry codes: (i) 0.5 − *x*, −0.5 + *y*, −*z*; (ii) 0.5 + *x*, −0.5 + *y*, *z*; (iii) 0.5 − *x*, −0.5 + *y*, 1 − *z*; (*) −*x*, *y*, −*z* [b] Calculated from the regression line Cu-OW1 = −0.0308 (180-N-Cu-N′) + 2.6956, taken from ref. 6.

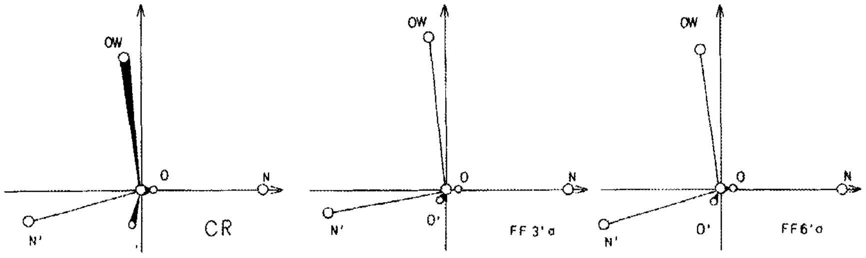

FIGURE 3 Copper coordination polyhedra obtained by two force fields. CR denotes the crystal structure.

The coordination polyhedron in the crystal lattice belonging to the type I polyhedra (*i.e.*, N-Cu-N′ > O-Cu-O′) is in accordance with the finding that all *N,N*-dimethylated derivatives have this form of coordination. Its shape resembles most that of the coordination polyhedron in aqua*bis(N,N*-dimethylglycinato-)copper(II), [24] differing only by $rms(\Delta\theta) = 1.1°$. Another alanine derivative, aqua*bis(L-N,N*-diethylalaninato)copper(II) [17] yielded a quite different shape (N-Cu-N′ < O-Cu-O′), differing from the *N,N*-dimethyl derivative by $rms^{Py} = 6.1°$. All force fields used (FF3'a, FF4'a, FF5'a, FF6'a) correctly reproduced the general shape of the coordination polyhedron (Fig 3).

The very short apical bond length [Cu-OW1 = 2.222(3) Å] is a consequence of a very high distortion of the coordination polyhedron. From the regression line correlating N-Cu-N′ angles with the apical bond lengths in the group I of molecules (regression No. 13) [6] the apical bond length in the title compound can be estimated to be Cu-OW1 = 2.271 Å. Due to the different shape of the coordination polyhedron obtained by molecular mechanics calculations, the estimation of the apical bond length from the same regression line gave 2.354 (FF3'a) and 2.218 Å (FF6'a).

From simple stereochemical reasoning it can be concluded that *bis(L-N,N*-dimethylalaninato)copper(II) has three conformers (*axial-axial, equatorial-equatorial* and *equatorial-axial*). Theoretical calculations (Table IV) showed that the most stable was the *a-a* conformer, but the energy difference from the most strained conformer (*e-e*) was only 2.67 kJ mol^{-1}. Aqua*bis(L-N,N*-dimethylalaninato)copper(II) has altogether six isomers due to two possible positions of the apically coordinated water (from C^{α}-CH_3 of C^{α}-H side of the molecule). Molecular mechanics calculations revealed that the bonding of a water molecule from the H-side is energetically favoured. The conformation obtained in the crystal (*e-e*, H-side) is not the most stable conformation; it is 1.42 kJ mol^{-1} higher in energy than the global minimum of the conformational potential (*i.e.*,

TABLE IV Relative conformational energy (kJ mol^{-1}) of the conformers of *bis(L-N,N*-dimethylalaninato)copper(II) and aqua*bis*(*L-N,N*-dimethylalaninato)copper(II)[a]

Conformer	$(Me_2Ala)_2Cu$	$(Me_2Ala)_2Cu\text{-}OH_2$	
		C^{α}-H side	C^{α}-R side
a-a	0.00	0.00	8.20
a-e	2.41	1.13	6.43
e-e	2.67	1.42*	2.78

[a] Calculations were performed with force field FF3'a. Zero point energies: 15.491 kJ mol^{-1} [$(Me_2Ala)_2Cu$] and 14.870 kJ mol^{-1} [$(Me_2Ala)_2Cu\text{-}OH_2$]. Conformation observed in crystal state is denoted with an asterix.

a-a H-side conformer). This result is not at all surprising because the crystal conformation does not appear to be the energetically most favoured one in *any* of the analyzed *N*-alkylated copper(II) aminoacidates so far. [17, 20-23, 25] Obviously, intermolecular interactions (extensive hydrogen bonding in the crystal lattice) appear to be the dominant factor determining the conformation of this class of molecules.

SUPPLEMENTARY MATERIAL

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

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References

[1] N. Paulić and N. Raos, *J. Coord. Chem.*, **31**, 181 (1994).
[2] J. Sabolović, N. Raos and Kj. Rasmussen, *Croat. Chem. Acta*, **62**, 495 (1989).
[3] J. Sabolović and N. Raos, *Polyhedron*, **9**, 1227 (1990).
[4] J. Sabolović and Kj. Rasmussen, *Inorg. Chem.*, **34**, 1221 (1995).
[5] N. Raos, *J. Mol. Struct.*, **355**, 211 (1995).
[6] N. Raos, *Croat. Chem. Acta*, **69**, 1189 (1996).
[7] R. E. Bowman and H. H. Stroud, *J. Chem. Soc.*, 1342 (1950).
[8] C. P. Nash and W. P. Schaefer, *J. Amer. Chem. Soc.*, **91**, 1319 (1969).
[9] Stoe & Cie, *STADI4. Diffractometer Control Program*, (Stoe, & Cie, Darmstadt, Germany, 1995).
[10] Stoe & Cie, *X-RED. Data Reduction Program*, (Stoe & Cie, Darmstadt, Germany, 1995).

[11] N. Walker and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).

[12] C. K. Johnson, *ORTEPII*, Report ORNL-5138, (Oak Ridge National Laboratory, Tennessee, USA, 1976).

[13] A. L. Spek, *PLUTON92*, Molecular Graphics Program, (University of Utrecht, The Netherlands, 1992).

[14] E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, **22**, 384 (1989).

[15] N. Raos, S. R. Niketić and Vl. Simeon, *J. Inorg. Biochem.*, **16**, 1 (1982).

[16] S. R. Niketić and Kj. Rasmussen *"The Consistent Force Field: A Documentation", Lecture Notes in Chemistry*, Vol. 3, (Springer-Verlag, Berlin, 1977); Kj. Rasmussen *"Potential Energy Functions in Conformational Analysis", Lecture Notes in Chemistry*, Vol. 37, (Springer-Verlag, Berlin, 1982); Kj. Rasmussen, S. B. Engelsen, J. Fabricius and B. Rasmussen, *"The Consistent Force Field: Development of Potential Energy Functions in Conformational Analysis", Recent Experimental and Computational Advances in Molecular Spectroscopy* (Proceedings of the NATO Advanced Study Institute on MOLECULAR SPECTROSCOPY, Ponta Delgada, Sao Miguel, Açores, Portugal, 1992), R. Fausto (Ed.), NATO ASI Series C: Mathematical and Physical Sciences, Vol. 406 (Kluwer Academic Publishers, Dodrecht, 1993), pp. 381-419.

[17] B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **25**, 337 (1992).

[18] B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 105 (1992).

[19] B. Kamenar, M. Penavić, A. Škorić, N. Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **17**, 85 (1988).

[20] B. Kaitner, E. Meštrović, N. Paulić and N. Raos, *J. Coord. Chem.*, **34**, 55 (1995).

[21] B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **30**, 233 (1993).

[22] B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 95 (1992).

[23] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer and A. G. Orpen, *J. Chem. Soc., Perkin Trans. II*, S1-S19 (1987).

[24] T. S. Cameron, K. Prout, F. J. C. Rossoti and D. Steele, *J. Chem. Soc., Dalton Trans.*, 2626 (1973).

[25] B. Kaitner, G. Pavlović, N. Paulić and N. Raos, *J. Coord. Chem.*, **36**, 327 (1995).