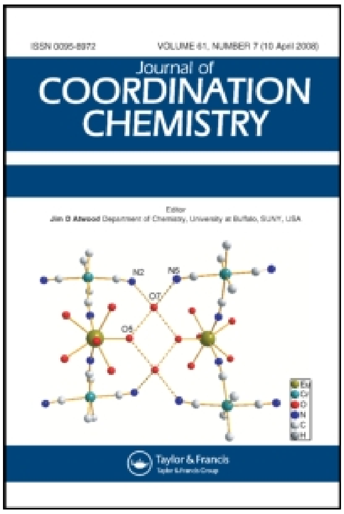

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STEREOCHEMISTRY OF COMPLEXES WITH N-ALKYLATED AMINO ACIDS. VIII. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF AQUA*BIS*(L-N,N-DIMETHYLTHREONINATO)COPPER(II) DIHYDRATE

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STEREOCHEMISTRY OF COMPLEXES WITH N-ALKYLATED AMINO ACIDS. VIII. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF AQUA*BIS*(L-N,N-DIMETHYLTHREONINATO)COPPER(II) DIHYDRATE

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The structure of blue, monoclinic (space group $P2_1$) crystals of aqua*bis(L-N,N*-dimethylthreoninato)copper(II) dihydrate was determined by X-ray diffraction and refined to $R = 0.030$. The coordination around the copper(II) atom is distorted square-pyramidal with threonine N and O atoms in *trans* orientations (Cu-O 1.930(3) and 1.926(3)Å, Cu-N 2.042(3) and 2.055(3)Å, O-Cu-O 163.9, N-Cu-N 164.0°) and apical water (Cu-O(W) 2.206 Å). 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 4.5°. The calculated strain energy of the crystal conformation is about 21 kJ mol^{-1} higher than the energy of the most stable conformer. This was tentatively attributed to the additional stabilization of molecular conformation by intermolecular hydrogen bonds in the solid state.

KEYWORDS: Copper(II), amino acids, *N,N*-dimethylthreonine, X-ray structure, conformation

INTRODUCTION

Copper(II) chelates with *N*-alkylated α-amino acids show very pronounced enantioselectivity effects[1] (not found for the complexes of naturally occuring amino acids[2]), used for the separation of enantiomers by ligand-exchange chromatography.[3] These copper(II) chelates with *N*-alkylated amino acids function very well as model compounds. Because of the lack of N—H bonds, there is a resultant paucity of NH—O hydrogen bonds, and therefore crystal structures

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resembling the hypothetical in *vacuo* state should be observed, especially in structures without apically bound water.[4,5] The presence of very large substituents on the nitrogen atom lead to distortion of the coordination polyhedron, which makes these copper(II) complexes nearly ideal model compounds for studying copper coordination.

In previous papers we developed novel molecular mechanics models for simulation of copper(II) distortion (they can be described as "dummy" atom models,[6,7] models with a distortion potential[8–10] and an electrostatic model[11]). The models were checked using copper(II) chelates with naturally occuring amino acids and their N-alkylated derivatives, and we have determined the crystal structures of these compounds.[4,5,12–16]

In this paper we describe the copper(II) chelate with *N,N*-dimethylthreonine, expecting distortion of coordination sphere to take place. Also, it is interesting to see how methylation influences coordination when comparing the *N*-methylated ligand with threonine.[17]

EXPERIMENTAL

L-N,N-Dimethylthreonine was synthesized by reductive methylation according to published procedures.[18] The preparation was carried out by condensation in 35% formaldehyde and subsequent hydrogenation over 10% Pd on activated charcoal during three days at room temperature. The ligand was purified by fractional crystallization from methanol/ether, yielding a white precipitate with m.p. 208–210°C. Its structure was confirmed by i.r., NMR and mass spectroscopy. The copper complex was prepared by reaction of the sodium salt of the ligand and copper(II) acetate monohydrate in CH_2Cl_2.[19] After slow evaporation, crystals suitable for X-ray analysis were obtained.

Crystal structure determination

$C_{12}H_{30}CuN_2O_9$, M_r = 409.92, monoclinic, space group $P2_1$, a = 7.781(1), b = 14.150(2), c = 8.643(1)Å, β = 97.33(1)°, V = 943.8(2)$Å^2$, Z = 2, D_x = 1.44 g cm^{-3}, $F(000)$ = 434, $\lambda(MoK\alpha)$ = 0.7093Å, $\mu(MoK\alpha)$ = 12.0 cm^{-1}.

A dark blue, prism-shaped crystal with approximate dimensions 0.37 × 0.32 × 0.24 mm was chosen for the X-ray study. Intensity data were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo*Kα* radiation, and a θ–2θ scan technique. Three standard reflections were monitored every 2 hours during data collection; there were no significant changes in intensity of the standard reflections. Cell parameters were obtained from the least-squares refinement of positions of 25 reflections in the range $24 < 2\theta < 40°$. Intensity data were collected in the 2θ range 4–54° with $-9 < h < 9$, $0 < k < 18$, $0 < 1 < 11$. Some 2260 intensity observations were collected; 2120 were unique with R_{int} = 0.012 for merging equivalent reflections; 1806 were considered as observed with $I > 2.5\ \sigma(I)$ and used in structure determination and refinement. Lorentz, polarization and absorption corrections were applied. The Gaussian numerical method was used for absorption correction with minimum and maximum transmission factors t_{min} = 0.751 and t_{max} = 0.822, respectively. The structure was solved by the heavy-atom method. Non-hydrogen atoms were located from subsequent difference Fourier syntheses and refined initially with isotropic and then with anisotropic thermal parameters. After several cycles of full-matrix least-squares anisotropic refinement, all hydrogen atoms belonging to the threonine ligands were calculated at ideal positions based on molecular geometry with C-H 0.95Å. These positions were constrained during subsequent refinement. The coordinates of the hydrogen atoms of the water molecules were obtained from a difference Fourier synthesis. Thermal parameters of all H atoms were constrained to the equivalent isotropic thermal displacement of the carbon and oxygen atoms to which they were bonded as $U_{iso}(H) = U_{eq}(C,O) \times 1.2$. The absolute configuration was established unequivocally by refinement of a $\delta f''$ multiplier. Final residuals were R = 0.030 and R_w = 0.036 (R = 0.034 and R_w = 0.041 for opposite hand) with $w = 1/[\sigma^2 F_o + 0.0004(F_o^2)]$, S = 1.20, $(\Delta/\sigma)_{max}$ = 0.009, maximum positive and negative electron densities in the final difference Fourier synthesis 0.25 and −0.22 eÅ^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography.*[20] Final atomic positional and equivalent ispotropic thermal parameters are listed in Table 1. Selected crystallographic bond distances, bond and torsion angles along with those calculated from the molecular mechanics calculations are listed in Table 2. An *ORTEP*II[21] view of the molecule in a general position showing the atom numbering scheme is

Table 1 Atomic fractional coordinates (x10^4, x10^5 for Cu) and thermal displacement parameters B_{eq} (Å^2).

	x/a	y/b	z/c	B_{eq}*
Cu	36715(5)	0	24117(5)	2.38(2)
011	5567(4)	614(2)	3683(3)	3.2(1)
012	7747(4)	1596(3)	3637(4)	4.3(2)
013	6118(4)	2151(2)	- 1138(3)	3.1(1)
021	1440(4)	- 298(2)	1286(3)	3.5(1)
022	- 1100(3)	- 938(2)	1446(4)	3.2(1)
023	547(4)	- 1671(2)	6145(3)	3.8(1)
0W1	5313(4)	- 1156(3)	1715(5)	5.0(2)
0W2	7561(7)	998(3)	6952(4)	6.5(2)
0W3	- 1792(6)	- 803(4)	8075(5)	6.6(2)
N1	4308(4)	920(3)	756(4)	2.8(1)
N2	2627(4)	- 610(2)	4237(4)	2.4(1)
C11	6558(5)	1132(3)	2959(5)	2.7(2)
C12	6190(5)	1124(3)	1170(4)	2.0(2)
C13	6891(5)	2009(3)	434(5)	2.5(2)
C14	8850(6)	1953(4)	487(5)	3.4(2)
C15	3878(7)	488(5)	- 830(5)	5.3(3)
C16	3245(6)	1776(5)	928(7)	5.4(3)
C21	422(5)	- 791(3)	1979(4)	2.3(2)
C22	1228(5)	- 1245(3)	3539(5)	2.3(2)
C23	- 197(6)	- 1522(3)	4555(5)	2.8(2)
C24	- 1154(6)	- 2409(4)	3951(6)	4.0(2)
C25	4001(6)	- 1102(4)	5297(5)	3.7(2)
C26	1940(6)	207(3)	5054(5)	3.4(2)

*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 (FF3a′)
Cu-O(11)	1.930(3)	1.952
Cu-O(21)	1.926(3)	1.954
Cu-OW(1)	2.206(3)	2.476
Cu-N(1)	2.042(3)	2.021
Cu-N(2)	2.055(3)	2.022
O(11)-C(11)	1.283(5)	1.274
O(21)-C(21)	1.262(5)	1.274
O(12)-C(11)	1.221(5)	1.240
O(22)-C(21)	1.232(5)	1.240
O(13)-C(13)	1.428(5)	1.423
O(23)-C(23)	1.437(5)	1.424
N(1)-C(12)	1.490(5)	1.481
N(2)-C(22)	1.479(5)	1.488
N(1)-C(15)	1.500(6)	1.484
N(2)-C(25)	1.488(6)	1.484
N(1)-C(16)	1.485(7)	1.481
N(2)-C(26)	1.489(5)	1.481
C(11)-C(12)	1.536(6)	1.525
C(21)-C(22)	1.552(6)	1.525
C(12)-C(13)	1.536(6)	1.563
C(22)-C(23)	1.550(6)	1.564
C(13)-C(14)	1.521(6)	1.552
C(23)-C(24)	1.517(7)	1.550
N(1)-Cu-N(2)	164.0(2)	173.0
O(11)-Cu-O(21)	163.9(2)	167.2
O(11)-Cu-OW(1)	93.6(1)	96.5
O(21)-Cu-OW(1)	102.5(1)	96.2
O(11)-Cu-N(1)	82.9(1)	85.6
O(21)-Cu-N(2)	82.9(1)	85.5
OW(1)-Cu-N(1)	94.7(2)	93.2
OW(1)-Cu-N(2)	101.4(2)	93.8
C(12)-N(1)-C(15)	113.3(3)	112.8
C(22)-N(2)-C(25)	113.6(3)	113.0
C(12)-N(1)-C(16)	111.2(4)	112.9
C(22)-N(2)-C(26)	112.0(3)	113.3
C(15)-N(1)-C(16)	111.2(4)	111.1
C(25)-N(2)-C(26)	110.1(3)	111.7
O(11)-C(11)-O(12)	122.6(4)	117.9
O(21)-C(21)-O(22)	123.1(4)	118.0
O(11)-C(11)-C(12)	116.1(3)	118.1
O(21)-C(21)-C(22)	115.6(3)	118.0
O(12)-C(11)-C(12)	121.3(4)	124.0
O(22)-C(21)-C(22)	121.2(4)	124.0
N(1)-C(12)-C(11)	107.1(3)	106.4
N(2)-C(22)-C(21)	107.3(3)	106.2
N(1)-C(12)-C(13)	116.6(3)	114.7
N(2)-C(22)-C(23)	117.7(3)	115.5
C(11)-C(12)-C(13)	112.4(3)	112.4
C(21)-C(22)-C(23)	111.0(3)	112.3
Cu-O(11)-C(11)	116.3(3)	111.3
Cu-O(21)-C(21)	117.4(3)	111.2
Cu-N(1)-C(12)	105.9(2)	104.0
Cu-N(2)-C(22)	106.5(2)	103.7
Cu-N(1)-C(15)	109.5(3)	109.0

Table 2 *Continued.*

Internal coordinate	Experimental value	Theoretical value (FF3a′)
Cu-N(2)-C(25)	110.2(3)	108.9
Cu-N(1)-C(16)	105.2(3)	106.5
Cu-N(2)-C(26)	103.8(2)	105.8
O(13)-C(13)-C(12)	112.3(3)	111.7
O(23)-C(23)-C(22)	110.4(3)	111.9
O(13)-C(13)-C(14)	109.5(3)	108.1
O(23)-C(23)-C(24)	109.1(3)	106.8
O(12)-C(13)-C(14)	110.6(3)	111.6
C(22)-C(23)-C(24)	111.7(4)	111.2
O(11)-C(11)-C(12)-N(1)	28.2(2)	39.2
O(21)-C(21)-C(22)-N(2)	30.2(2)	40.1
N(1)-Cu-O(11)-C(11)	- 13.4(2)	- 5.4
N(2)-Cu-O(21)-C(21)	- 7.4(2)	- 5.8
O(11)-Cu-N(1)-C(15)	150.1(3)	146.0
O(21)-Cu-N(2)-C(25)	147.1(3)	146.7
Cu-O(11)-C(11)-C(12)	- 5.0(1)	- 17.4
Cu-O(21)-C(21)-C(22)	- 10.8(1)	- 17.6
Cu-N(1)-C(12)-C(13)	- 162.1(4)	- 162.6
Cu-N(2)-C(22)-C(23)	- 158.7(4)	- 164.0
N(1)-C(12)-C(13)-C(14)	- 160.6(5)	- 169.4
N(2)-C(22)-C(23)-C(24)	- 160.2(5)	- 168.7
H(13)-O(13)-C(13)-C(12)		- 65.7
H(23)-O(23)-C(23)-C(22)		99.0

given in Figure 1. All calculations were performed on a Silicon Graphics 4D-380 computer using the *NRCVAX* crystallographic computing program package.[22]

Conformational analysis

The theoretical conformation analysis was based upon the minimsation of the conformational (strain) potential energy, ϕ_T, computed from the empirical formula *(1)*.

$$\phi_T = \frac{1}{2}\sum_i k_{d,i}(d_i - d_{o,i})^2 + \frac{1}{2}\sum_j k_{\theta,j}(\theta_j - \theta_{o,j}) + \\ + \sum_k \phi_k(1 \pm cos\, n_k\gamma_k) + \sum_l (A_l\, exp(-B_l r_l) - C_l r_l^{-6}) + \\ + \frac{1}{2}\sum_m k_{\chi,m}\chi^2 \qquad (1)$$

In this equation d, θ and γ stand for bond lengths, valence and torsional angles, respectively, r is the 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_k and n, and non-bonded intractions were computed from a Buckingham function with parameters A, B and C. In addition, in the force field denoted with *a* (FF2a *etc.*) the out-of plane torsion potential for the carboxyl group was also computed using the function with an empirical parameter k_χ and the out

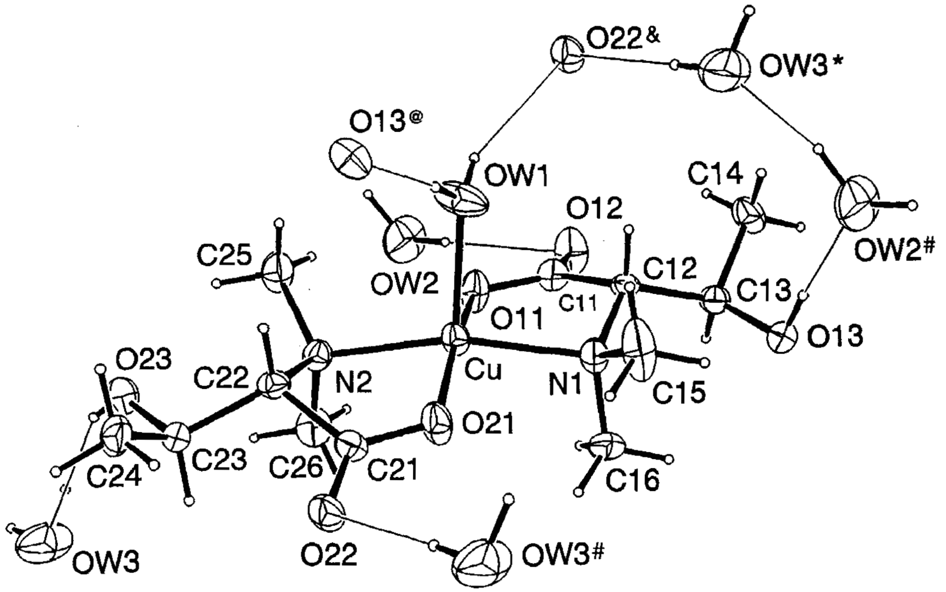

Figure 1. An *ORTEP*II diagram of aqua*bis(L-N,N*-dimethylthreoninato)copper (II) dihydrate in a general position showing the crystallographic numbering scheme and hydrogen bonding. Ellipsoids are drawn at the 35% probability level. Symmetry codes: (@) $-x+1$, $y-0.5$, $-z$; (*) $x+1$, y, z; (#) x, y, $z-1$.

of plane angle χ. The overall description of force fields was given elsewhere.[5] Calculations were performed with the program developed by Kj. Rasmussen and co-workers.[23]

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

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

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

RESULTS AND DISCUSSION

The compound crystallizes as a mono-aqua complex with two water molecules in the asymmetric unit. The copper atom coordination is distorted square pyramidal with oxygen and nitrogen atoms in *trans* positions in the equatorial plane and with the coordinated water molecule apical. The molecules are linked *via* O-H. . .O hydrogen bonds ranging in length from 2.662(5) to 3.008(5)Å. Coordinated water molecule OW1 and hydroxyl 013 and 023 oxygen atoms act as proton donors only while crystal water molecules OW2 and OW3 act both as proton donors and proton acceptors (Fig. 1). The observed Cu-O bond distances 1.926(3) and 1.930(3)Å are very similar to those found in aqua*bis*(N-tert-butyl-N-methylglycinato)copper(II)[15] and aqua*bis(L-N,N*-diethylalaninato)copper(II)[14][1.922(2)Å] although corresponding distances in aqua*bis(L-N,N*-dimethylisoleucinato)copper(II)[12] differ significantly [1.900(5) and 1.949(5)Å, respectively]. The average Cu-N bond distance [value 2.049(4)Å] is intermediate between those observed in abovementioned *N,N*-diethylalaninato [2.075Å],[14] *N-tert*-butyl-*N*-methylglycinato [2.081(2)Å][15] and *N,N*-dimethylisoleucinato complexes [2.014(5) and 2.019(5)Å, respectively].[12] The copper atom coordination polyhedron has a very short Cu-OW1 bond distance of 2.206(3)Å. This value is shorter than found in abovementioned complexes, which range from 2.260(4)Å [*N,N*-diethylalanianto derivative] to 2.464(2)Å [*N-tert*-butyl-*N*-methylglycinato derivative]. The displacement of the Cu atom is 0.277Å out of the 011, 021, N1, N2 best fit plane, towards the OW1 water molecule, causing the O-Cu-O and N-Cu-N bond angles to be displaced from linearity (163.9(2) and 164.0(2)°, respectively). Hydrogen bonding appears to have no influence on the open envelope conformation of the two threonine ligands with essentially identical N1-C12-C13-C14 [160.6(5)°] and N2-C22-C23-C24 [160.2(5)°] torsion angles (3σ criterion). No correlation can be made between our observed molecular geometery parameters and molecular geometry and dimensions reported for the crystal structure of *bis(L*-threoninato)copper(II) monohydrate[17] where the Cu atom has 4 + 2 coordination with two asymmetrically positioned carboxyl atoms from the adjacent molecules in apical positions with Cu-O bond lengths 2.48 and 2.94Å, respectively.

Comparison of the crystal structure with the structures obtained by molecular mechanics calculations (Figs. 2 and 3, Table 2) revealed that the best reproduction was obtained with force field FF3a′. Also, it is evident from Figure 3 that force fields which include interactions with apically pleced water (those marked with a prime) yielded a generally better reproduction of both the overall crystal structure [expressed as $\varepsilon_{\mathrm{r.m.s.}}(\Delta r)$] and the shape of copper coordination polyhedron [expressed as $\varepsilon_{\mathrm{r.m.s.}}(\Delta\theta)$]. Polyhedra obtained with force field marked with a prime (column FF3a′, Fig. 3) yielded generally structures which are closer to each other than to the crystal structure. Also, all theoretical structures have a less distorted coordination polyhedron than that obtained experimentally (column Py, Fig. 3). The obvious explanation of this finding is that there are additional factors which determine the final shape of the coordination polyhedron in the crystal structure, mainly intermolecular interactions, especially hydrogen bonding.

The overall conformational analysis of the title compound is also consistent with the finding that there are pronounced intermolecular interactions in the crystal lattice. The conformer with the lowest conformational potential (6–6; Tables 3 and 4) does not correspond to the crystal conformation. On the contrary, the crystal structure corresponds to the conformer denoted as 14–15 which is 21.34 kJ mol^{-1} higher in energy than the global minimum. This is different to what was observed for *N,N*-dialkylated amino acids with hydrophobic side chains for which the most stable conformer was identical with the conformation in the crystal.[4,5,13]

Our findings are consistent with the actual conformation in the crystal lattice being mainly determined by the presence of signficant intermolecular interactions, such as hydrogen bonding.

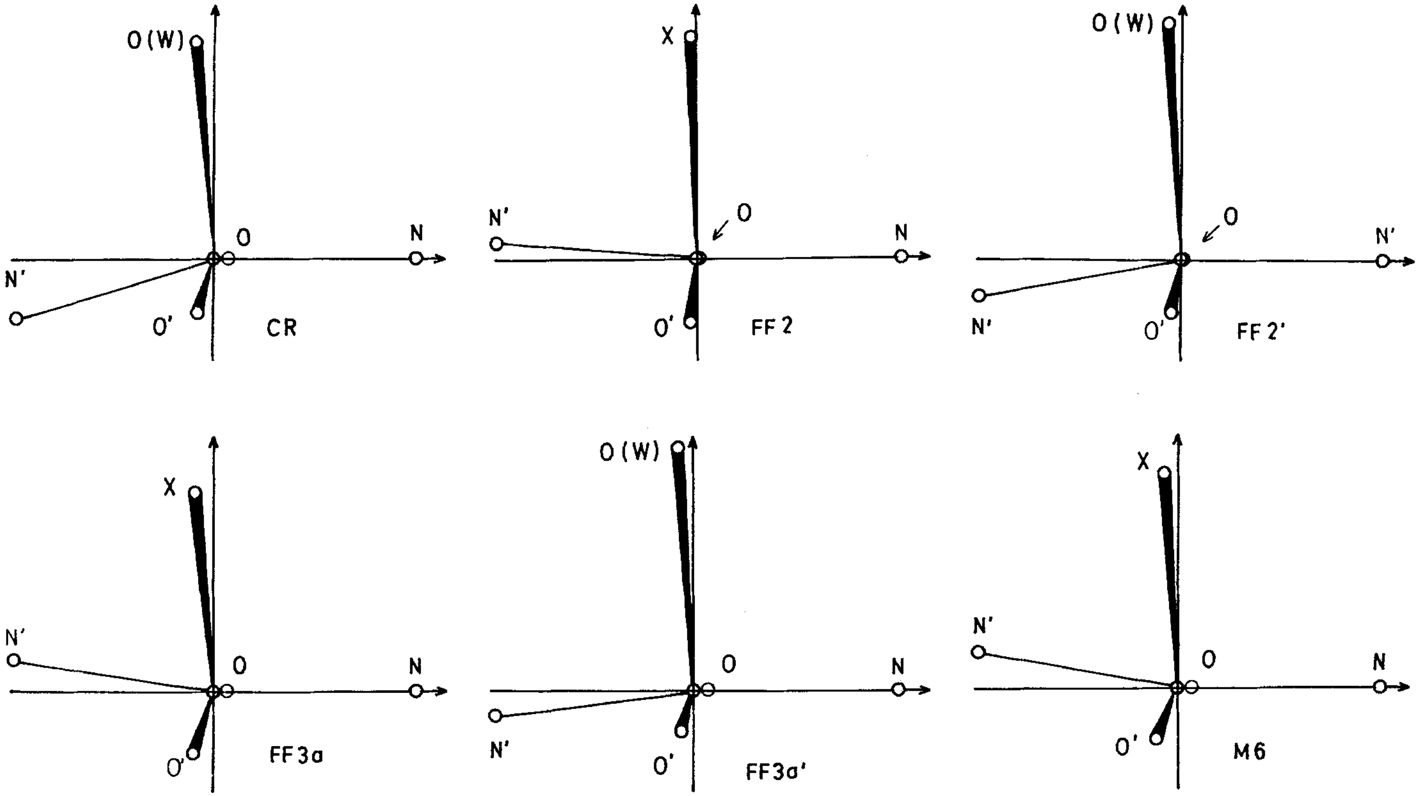

Figure 2. Copper coordination polyhedron obtained by five force fields. Force fields marked with a prime have assigned non-bonded potential to O(w). X denotes the position of a "dummy" atom, *i.e.*, O(w) without non-bonded intractions with the rest of the molecule. CR denotes crystal conformation.

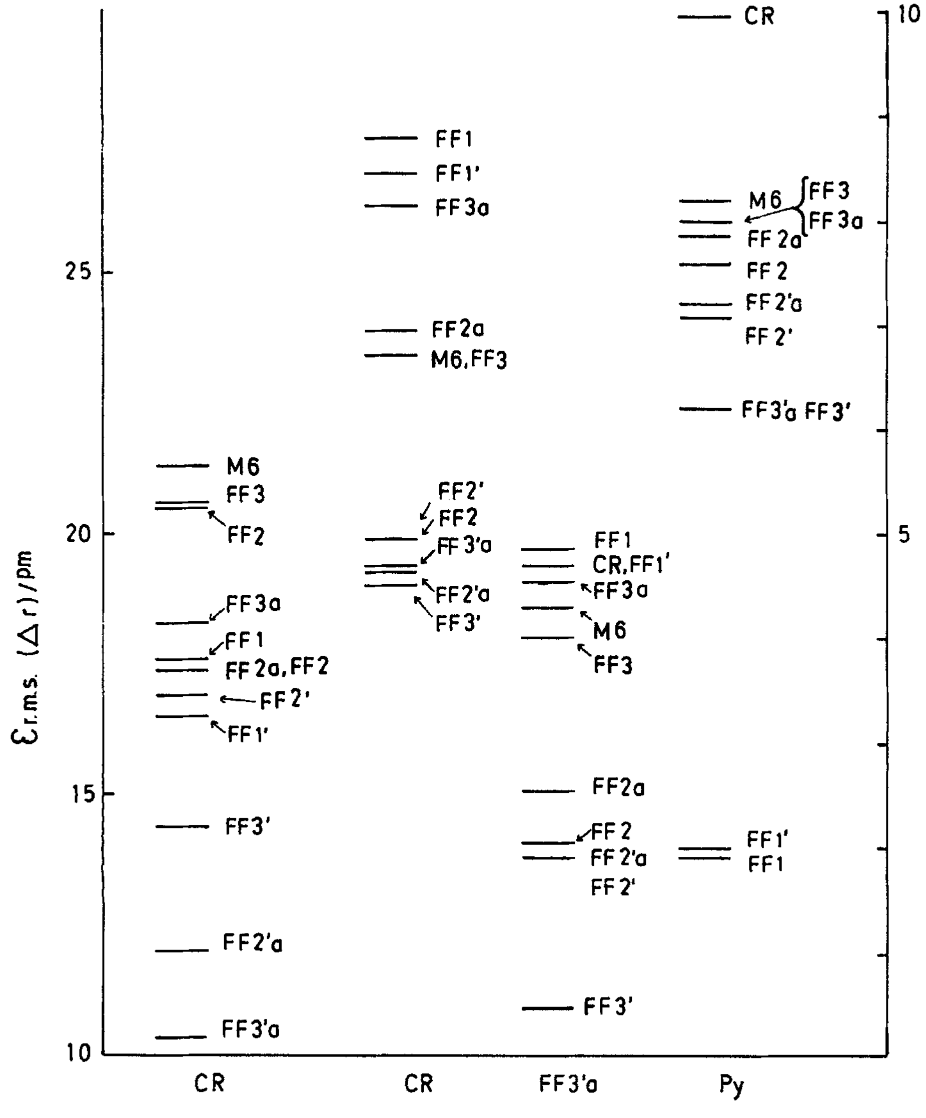

Figure 3. Comparison of the X-ray molecular structure with the theoretically predicted conformations. CR: molecular conformation in the crystal; FF1, FF2 *etc.*; conformations obtained with respective force fields; $\varepsilon_{r.m.s}(\Delta r)$ were computed neglecting H atoms; $\varepsilon_{r.m.s.}(\Delta\theta)$ refers to ten valence angles defining the geometry of copper coordination.

Supplementary data

Full lists of anisotropic thermal parameters, hydrogen coordinates, observed and calculated structure factors, bond lengths and angles, and torsion angles are available from the authors upon request.

Table 3 Chelate ring conformations of bis(*L*-*N*,*N*-diemthylthreoninato)aquacopper(II)*.

	Ring conformation	γ_1	γ_2	ϕ_T(kJ mol^{-1})
1	axial	-64.71	65.54	2.00
2	axial	84.61	-67.06	10.38
3	axial	14.96	64.89	17.32
4	axial	84.62	-177.57	10.31
5	axial	-63.43	-62.84	0.84
6	axial	-168.33	59.84	0.00
7	axial	-168.28	-174.66	0.36
8	equatorial	-53.63	-83.82	16.16
9	equatorial	-61.04	65.10	8.60
10	equatorial	-58.54	177.30	6.89
11	equatorial	74.25	64.27	14.63
12	equatorial	84.31	-61.73	15.00
13	equatorial	76.13	147.36	15.11
14	equatorial	-168.99	-64.96	3.01
15	equatorial	-169.53	93.86	9.91
16	equatorial	-166.04	175.24	2.55

*Zero point of conformational potential, ϕ_{TO} = 17.19765 kJ mol^{-1}. Torsion angles γ_1 and γ_2 correspond to angles N1-C12-C13-O13 and H13-O13-C13-C12, respectively.

Table 4 Conformational energy (kJ mol^{-1}) of selected stable conformations of *bis(L-N,N*-dimethylthreoninato)copper(II) and aqua*bis(L-N,N*-dimethylthreoninato)copper(II)*.

Conformer		$(Me_2Thr)_2Cu$	$(Me_2Thr)_2Cu.H_2O$	
			Side A	Side B
1	1	4.54	38.40	11.39
1	4	12.19	39.72	15.76
1	5	3.66	36.86	10.35
1	6	0.93		9.99
1	7	0.81		4.45
1	9	11.44	29.11	15.19
1	10	11.12	27.48	13.50
1	14	4.84		9.11
1	15	11.05		15.99
1	16	4.57		8.33
4	4	20.48	43.05	21.68
4	5	11.37	38.20	14.66
4	7	9.90	26.62	10.50
4	9	22.01	33.55	23.21
4	10	21.71	31.99	21.70
4	14	15.53	27.98	17.82
4	15	21.70	34.80	24.49
4	16	15.24	27.19	16.86
5	5	2.79	35.77	9.33
5	6	0.11		8.74
5	7	0.00	21.58	3.31
5	9	10.59	27.62	13.96
5	10	10.28	25.99	12.27
5	14	3.99		7.88
5	15	10.20	28.74	14.76
5	16	3.72		7.10
6	4	11.62	22.20	16.78

Table 4 *Continued.*

Conformer	$(Me_2Thr)_2Cu$	$(Me_2Thr)_2Cu.H_2O$	
		Side A	Side B
6 6	0.46	0.00	10.35
6 7	2.41	6.78	6.71
6 9	11.49	12.65	16.94
6 10	11.13	11.02	15.40
6 14	4.95	6.97	11.22
6 15	11.20	13.87	17.98
6 16	4.75	6.33	10.39
7 7	0.84	11.01	0.45
7 9	13.02	19.00	13.70
7 10	12.70	17.48	12.20
7 14	6.50	13.64	8.47
7 15	12.68	20.37	15.02
7 16	6.23	12.72	7.47
9 9	22.43	24.70	26.53
9 10	22.06	23.07	24.96
9 14	15.69	19.05	20.74
9 15	21.98	25.86	27.34
9 16	14.70	18.29	19.79
10 10	21.68	21.43	23.35
10 14	15.31	17.40	19.05
10 15	21.60	24.22	25.70
10 16	15.10	16.65	18.16
14 14	8.95	13.37	14.57
14 15	15.25	20.21	21.34
14 16	8.75	12.65	13.87
15 15	21.54	27.04	28.05
15 16	15.05	19.48	20.52
16 16	8.55	11.91	13.00

*Sides, *A* and *B* correspond to C^{α}-R and C^{α}-H sides of the chelate ring, respectively. Zero points: 875.50 kJ mol^{-1}[$(Me_2Thr)_2Cu$] and 21.19 kJ mol^{-1}[$(Me_2Thr)_2Cu.H_2O$]. For missing values, conformational energy was impossible to obtain by minimization. Only conformations composed of chelate rings with $\phi_T < 10$ kJ mol^{-1} are presented.

References

1. V.A. Davankov, S.V. Rogozhin and A.A. Kurganov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **204A** (1971); V.A. Davankov, S.V. Rogozhin and A.A. Kurganov, *Zh. Neorg. Khim.*, **17**, 2163 (1972).
2. R.D. Gillard, H.M. Irving, R.M. Parkins, N.C. Payne and L.D. Pettit, *J. Chem. Soc. A*, 1159 (1966); Vl. Simeon and O.A. Weber, *Croat. Chem. Acta*, **38**, 161 (1966); D.S. Barnes and L. D. Pettit, *J. Inorg. Nucl. Chem.*, **33**, 2177 (1971).
3. V.A. Davankov and A.V. Semechkin, *J. Chromatogr.*, **141**, 313 (1977).
4. B. Kaitner, B. Kamenar, N. Paulić and Vl. Simeon, *J. Coord. Chem.*, **15**, 373 (1987).
5. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **22**, 269 (1991).
6. N. Raos, S.N. Niketić and Vl. Simeon, *J. Bioanorg. Chem.*, **15**, 1 (1982)
7. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **58**, 127 (1985).
8. J. Sabolović, N. Raos and Kj. Rasmussen, *Croat. Chem. Acta*, **62**, 495 (1989).
9. J. Sabolović and N. Raos, *Polyhedron*, **9**, 1277 (1990).
10. J. Sabolović, N. Raos and Kj. Rasmussen, *Polyhedron*, **10**, 2079 (1991).
11. J. Sabolović and N. Raos, *Polyhedron*, **9**, 2419 (1990).
12. B. Kamenar, M. Penavić, A. Škorić, N Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **17**, 85 (1988).
13. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 105 (1992).
14. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **25**, 337 (1992).

15. B Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 95 (1992).
16. B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, submitted for publication.
17. V. Amirthalingam and K.V. Muralidharan, *Pramana*, **4**, 83 (1975).
18. H. Brockmann, H.B. Konig and R. Oster, *Chem. Berichte*, **6**, 865 (1954).
19. C.P. Nash and W.P. Schaefer, *J. Amer. Chem. Soc.*, **91**, 1319 (1969).
20. *"International Tables for X-ray Crystallography,"* Vol. IV, (Kynoch Press, Birmingham, 1974). Present distributor: Kluwer Academic Publishers, Dordrecht, the Netherlands.
21. C.K. Johnson, "*ORTEP*II," Report ORNL-5138, Oak Ridge National Laboratory, Tennssee, USA (1976).
22. E.J. Gabe, Y. Le Page, J-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.*, **22**, 384 (1989).
23. S.R. Niketić and K. Rasmussen, *"The Consistent Force Field: A Documentation"*, (Springer-Verlag, Berlin, 1977); K. Rasmussen, *"Potentional Energy Functions in Conformational Analysis"*, (Springer-Verlag, Berlin, 1985).