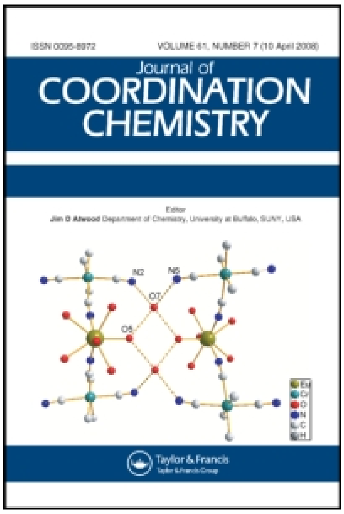

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Stereochemistry of Complexes with *N*-Alkylated Amino Acids. VI. Crystal Structure of *BIS*(*N-Tert*-Butyl-*N*-Methylglycinato)Aquacopper(II). Conformational Analysis and Molecular Mechanics Calculations

B. Kaitner[a]; G. Ferguson[a]; N. Paulić[b]; N. Raos[b]
[a] Department of Chemistry and Biochemistry, University of Cuelph, Guelph, Ontario, Canada [b] Laboratory for Analytical and Physical Chemistry, Institute for Medical Research and Occupational Health, University of Zagreb, Zagreb, Croatia, Yugoslavia

To cite this Article Kaitner, B. , Ferguson, G. , Paulić, N. and Raos, N.(1992) 'Stereochemistry of Complexes with *N*-Alkylated Amino Acids. VI. Crystal Structure of *BIS*(*N-Tert*-Butyl-*N*-Methylglycinato)Aquacopper(II). Conformational Analysis and Molecular Mechanics Calculations', Journal of Coordination Chemistry, 26: 2, 95 — 104

To link to this Article: DOI: 10.1080/00958979209407918

URL: http://dx.doi.org/10.1080/00958979209407918

J. Coord. Chem. 1992, Vol. 26. pp. 95–104
Reprints available directly from the publisher
Photocopying permitted by license only

STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. VI. CRYSTAL STRUCTURE OF *BIS*(*N*-*TERT*-BUTYL-*N*-METHYLGLYCINATO)AQUACOPPER(II). CONFORMATIONAL ANALYSIS AND MOLECULAR MECHANICS CALCULATIONS

B. KAITNER‡*, G. FERGUSON

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

N. PAULIĆ and N. RAOS

Laboratory for Analytical and Physical Chemistry, Institute for Medical Research and Occupational Health, University of Zagreb, Zagreb, Croatia, Yugoslavia

(*Received 18 November 1991*)

The structure of blue, orthorhombic crystals of *bis*(*N*-*tert*-butyl-*N*-glycinato)aquacopper(II) was solved by X-ray diffraction method and refined to $R = 0.026$. The copper atom has a distorted square-pyramidal coordination with two nitrogen atoms and two oxygen atoms in *trans* positions in the equatorial plane and an apically coordinated water molecule. The structure is built up of discrete molecules linked together *via* C=O···H–OH hydrogen bridges. The Cu–O [1.922 (2)Å], Cu–N [2.081 Å(2)] and Cu–OW [2.464 (2)Å] distances are comparable with those of copper(II) complexes with other α-amino acids. The conformation of the molecule corresponds to the most stable conformer predicted theoretically.

Keywords: Copper(II), *bis*(*N*-*tert*-butyl-*N*-methylglycinato)copper(II), *bis*(*N*-*tert*-butyl-*N*-methylglycinato)-aquacopper(II), X-ray structure, conformation, molecular mechanics

INTRODUCTION

Bis-chelates of *N*-alkylated and *N*,*N*-dialkylated α-amino acids with copper(II) and other transition metals can be discussed with respect to two kinds of dominant steric interactions. The first kind of interactions was studied as early as 1954 when it was found that the size of alkyl residue bound to glycine nitrogen had an influence on the stability of ML and ML_2 complexes with copper(II) and nickel(II).[1] From the other side, in the copper(II) chelates with *N*-alkylated prolinates, valinates and isoleucinates, dominant steric interactions appear to be caused by the close approach of bulky groups bound to the C^α-atom.[2,3] The study of the latter group of the chelates led to the discovery of the enantioselectivity effect in the class of tetracoordinated chelates of amino acids[4,5] and to its imminent application—ligand-exchange chromatography for resolution of racemic amino acids.[6]

Having the principal goal to develop a molecular mechanical model for conformational analysis of copper(II) chelates with amino acids, peptides and other

---

* Author for correspondence.

‡ On leave from University of Zagreb.

naturally occurring ligands, we found that *N*-alkylated and *N,N*-dialkylated amino acids were the ligands very well suited for that purpose. Because of the close approach of bulky groups, very severe distortion of copper(II) coordination polyhedron takes place both in tetracoordinated[7,8] and pentacoordinated aqua-complexes.[9,10] Moreover the distortion of coordination polyhedron is closely connected with the stability of the complex and, as a consequence, with the enantioselectivity.[2,11–14] Only if the distortion of the copper(II) coordination sphere was taken into account, was it possible to properly reproduce the observed enantioselectivity in the *N,N*-dimethylvaline/copper(II) system.[11]

In this paper we deal with a molecule specially designed in order to study the influence or bulky *tert*-butyl group on the apical coordination of water and on the shape of coordination polyhedron.

EXPERIMENTAL

The ligand, *N*-*tert*-butyl-*N*-methylglycine was prepared by a two-step procedure. *N*-*tert*-butylglycine was prepared by reaction of *tert*-butylamine with ethyl-ester of monobromoacetic acid, with subsequent saponification.[15] The sodium salt was converted to the acid (by addition of HCl to pH = 2) which was then isolated by fractional crystallization from aqueous solution and subsequently purified by recrystallization from absolute ethanol/ether mixture (m.p. = 212–215°C; total yield 33%). The ligand *N*-*tert*-butylglycine was methylated by condensation with formaldehyde followed by hydrogenation over Pd/C[16] (72 hr, 1.5 bar, room temperature). After recrystallization from ethanol, a white powder was obtained (m.p. = 204–205°C; yield 90%, total yield 30%). The materials were characterised by mass spectroscopy and nitrogen analysis. The complex was prepared by reaction of copper(II) acetate monohydrate and sodium salt of the acid in CH_2Cl_2 solution.[17]

Crystal structure determination

Crystal data:
$C_{14}H_{30}CuN_2O_5$, $M_r = 369.95$, orthorhombic, space group $P2_12_12$, $a = 7.565(1)$, $b = 9.378(2)$, $c = 12.171(2)$ Å, $V = 863.5$ Å^3, $Z = 2$, $D_x = 1.42$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0.7093$ Å, $\mu = 12.9$ cm^{-1}, $F(000) = 394$.

Crystals suitable for X-ray structure determination were recrystallized from benzene. A dark blue crystal (0.36 × 0.35 × 0.15 mm) was used for intensity measurements. The cell parameters were determined from the refinement of setting angles of 25 reflections in the 2θ range 10 to 38° on an Enraf-Nonius CAD-4 single crystal diffractometer using graphite-monochromated Mo *Kα* radiation. Data collection was by the ω-2θ technique with $4 \leqslant 2\theta \leqslant 54°$. Intensities of three standard reflections, monitored throughout the data collection, were constant within experimental error. In all we collected 3899 reflections in the index range $-9 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 12$, $-15 \leqslant l \leqslant 15$, *i.e.*, four octants. Corrections were made for Lorentz and polarization factors but not for absorption. A secondary extinction correction was applied during refinement. After merging and averaging of equivalent reflections ($R_{int} = 0.015$) we were left with 1891 reflections with hkl and $hk\bar{l}$ indices (for use in anomalous dispersion determination of absolute stereochemistry). Of these reflections the 1585 with $I \geqslant 2.5\sigma(I)$ were labelled "observed" and used in subsequent calculations. The space group $P2_12_12$ was determined uniquely from the systematic absences ($h00$, $h=2n+1$; $0k0$, $k=2n+1$). The molecule has twofold crystallographic symmetry with the Cu atom and water molecule on a twofold axis. The structure was solved by the heavy-atom method; the position of the copper atom was found from a Patterson map and subsequent difference Fourier syntheses revealed the complete structure. Refinement was by full-matrix least-squares methods with non-hydrogen atoms allowed anisotropic thermal motion. The hydrogen atoms were placed in their expected geometrical position (C–H 0.95 Å); the water molecule H atom was found from a difference Fourier map calculated at $R=0.033$. Hydrogen atoms were included in structure factor calculations but not refined. The weighting scheme was $w=1/[\sigma^2(F_0)+0.034(F_0^2)]$. Parallel calculations with the opposite enantiomorph converged with a higher R factor (0.040) showing that the model chosen did indeed have the correct absolute stereochemistry (in agreement with known absolute stereochemistry). The refinement converged with $R=0.026$, $R_w=0.034$, and $S=0.94$. The largest shift in the last refinement cycle was less than 0.001, and the maximum electron density in the final difference Fourier synthesis was 0.30 eÅ^{-3}. All calculations were carried out with SDP-Plus on the PDP11/73 computer.[18] Atomic scattering and anomalous dispersion coefficients were taken from the *International Tables for X-ray Crystallography*, Vol. IV.[19] Final atomic coordinates and equivalent isotropic thermal displacement factors are given in Table I. Experimental bond lengths, bond angles and selected torsion angles are listed in Table II along with the predicted ones. Figure 1 shows the molecular structure and the atom numbering scheme used.

Lists of bond lengths, bond and torsion angles, anisotropic thermal parameters, calculated hydrogen coordinates and observed and calculated structure factors have been deposited with the Journal. Copies may be obtained from the Editor on request.

TABLE I

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

	x/a	y/b	z/c	B_{eq}*
Cu	0	0	−18661(3)	2.023(5)
OW	0	0	158(2)	3.69(5)
O1	1896(2)	−1363(2)	−1858(2)	2.76(3)
O2	2443(3)	−3626(2)	−1430(2)	3.71(4)
N	−1633(2)	−1779(2)	−1992(2)	2.03(3)
C1	1434(3)	−2629(2)	−1579(2)	2.56(4)
C2	−552(3)	−2855(2)	−1395(2)	2.49(4)
C3	−3273(3)	−1518(3)	−1368(3)	3.14(5)
C4	−2061(3)	−2233(3)	−3168(2)	2.79(4)
C5	−3453(4)	−3417(3)	−3201(3)	4.34(6)
C6	−2688(5)	−932(3)	−3796(2)	4.41(6)
C7	−406(4)	−2801(3)	−3737(2)	3.98(7)

*The form of the isotropic equivalent thermal parameter is

$$(4/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+ab\cos\gamma B_{12}+ac\cos\beta B_{13}+bc\cos\alpha B_{23})].$$

Conformational analysis

The conformational potential was calculated from basic formula (*1*),

$$\phi=\tfrac{1}{2}\sum_{i}k_{d,i}(d_i-d_{i,o})^2+\tfrac{1}{2}\sum_{j}k_{\theta,j}(\theta_j-\theta_{o,j})^2+\tfrac{1}{2}\sum_{k}\phi_n(1\pm\cos n\varphi_k)$$
$$+\sum_{l}(A_l\exp(-B_lr_l)-C_lr_l^{-6})+\tfrac{1}{2}\sum_{m}k_{\chi,m}\chi_m^2+\tfrac{1}{2}k_\beta(\beta-\beta_o)^2+\phi_{cis}+\phi_{trans}+\phi_{el}. \quad (1)$$

where d, θ, φ and χ stand for bond lengths, valence, torsion and out-of-plane angles, respectively; r is non-bonded distance. The 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 torsion 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 with a quadratic function dependent of parameter k_χ was also taken into account.

The last four terms in equation (*1*) correspond to interactions specific for copper coordination polyhedron. We altogether proposed three kinds of models. They are a "dummy" atom model (FF1–FF3a),[9,20] a model with distortion potential (M3–MM5)[12,13] and an electrostatic model (M6).[14] The quadratic potential dependent on distortion coordinate β and parameters β_o and k_β is specific for force fields M3–M5. The potentials ϕ_{cis} and ϕ_{trans} are angle-bending potentials for the angles around copper, which can be quadratic (a "dummy" atom model and M3) or in the form of cosine power series (M4, M5). The ϕ_{el} is the coulombic potential between the charges situated around the copper atom (M6).

For pentacoordinated aqua-complexes only "dummy" atom models were used. Those force fields can be grouped into "weak" (FF2–FF3a) and "strong" (FF1) ones because of large differences in values of k_{N-Cu-O} parameters. Also, they can be described as symmetrical force fields (FF1, FF3, FF3a), with equal parameters for all *cis* angles and asymmetrical ones (FF2, FF2a) with the subsequently weaker k_θ parameters for the apically situated ligand. The force fields denoted with a prime (*e.g.* FF2′) have an additional non-bonded potential with the apically situated atom, and in the force fields denoted with *a* (*e.g.*, FF2a) the potential ϕ_χ was also included.

A short overlay of models and parameters was given elsewhere.[8] Calculations were performed with a programme developed by K. Rasmussen and coworkers.[21]

Similarity between the structures was expressed with root-mean-square deviation (*2*),

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

where X stands for valence angles around copper when comparing the copper coordination geometry, or the interatomic distance r, when checking the overall similarity (only non-hydrogen atoms are taken into account). Δ denotes the difference between the values of the observable X in two structures.

RESULTS AND DISCUSSION

The molecule lies in the special position 2(*a*) of the space group with a two-fold axis passing through the copper and water molecule oxygen atom. The copper atom

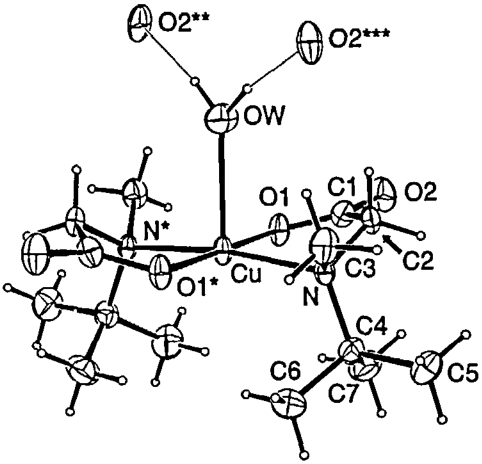

FIGURE 1 An *ORTEP*II (Johnson, 1976) drawing of the molecule showing the hydrogen bonding between the water molecule and the carbonyl oxygen atom and our crystallographic numbering scheme. The ellipsoids are drawn at the 35% probability level. Symmetry codes: (*) $-x$, $-y$, z; (**) $0.5-x$, $0.5+y$, $-z$; (***) $-0.5+x$, $-0.5-y$, $-z$.

coordination is distorted square-pyramidal with water molecule in apical position and with oxygen and nitrogen atoms in the equatorial plane in *trans* positions (Figure. 1). The five-membered chelate ring has an envelope conformation [torsion angle Cu-O1-C1-C2 4.8(3)°] with the N atom 0.64 Å from the Cu, O1, C1, C2 plane. The bond distances involving copper, oxygen and nitrogen atoms are as follows: Cu-OW 2.464(2), Cu-O1 1.922(2) and Cu-N 2.081(2) Å. The same Cu-O(ligand) bond distance is found in the copper complexes with *L-N,N*-dimethylisoleucine and with *D,L-N,N*-diethylalanine [$1.925(5)_{av}$ and 1.911(2) Å, respectively].[9,10] Although the bond angle O1-Cu-O1* is 179.40(8)° and OW-Cu-O is 89.70(6)° other bond angles between atoms included in the copper coordination sphere are depart significantly from 180° or 90° [N-Cu-N* 171.55(8)°, Ow-Cu-N 94.23(5)°, O-Cu-N angles in the equatorial plane 84.85(7) and 95.19(7)°]. In spite of this the distortion of the copper coordination polyhedron is less than in the abovementioned isoleucinato and alaninato copper complexes where corresponding O-Cu-O and N-Cu-N bond angles range from 159.9(2) to 175.6(1)°, and O(W)-Cu-O and O(W)-Cu-N from 83.4(2) to 101.0(2)°. We attribute the smaller distortion of our molecule to the presence of the bulky *tert*-butyl substituents on the nitrogen atoms which do not allow the water and surrounding molecules linked to it *via* OW-H···O2 hydrogen bonds [2.793(2) Å] to cause a major distortion of the copper coordination. The Cu atom is 0.072 Å out of the least-squares plane through the O1, O1*, N and N* atom towards OW.

The structure obtained experimentally corresponds to the conformer with the lowest strain energy (aRaR, Table II).

Interestingly, the binding of water to the apical position influences the energetical preference of the conformers by making the conformer aRaS less stable than conformer aRaR. Nevertheless, both conformers (aRaR and aRaS) have very close energy in

---

* Values (°): 179.64 and 177.32 (FF1'), 179.88 and 169.65 (FF2'), 179.89 and 169.46 (FF2'a), 179.37 and 169.67 (FF3'a), for N-Cu-N* and O1-Cu-O1* angle, respectively.

TABLE II
Relative conformational energy, ϕ, of the conformers of *bis*(*N-tert*-butyl-*N*-methylglycinato)aquacopper(II) (FF2', FF3'a) and *bis*(*N-tert*-butyl-*N*-methylglycinato)copper(II) (FF2, FF3a, M6) obtained with five force fields.*

	ϕ (kJ mol^{-1})				
Conformer	FF2'	FF2	FF3'a	FF3a	M6
aRaR	0.00	0.76	0.00	0.92	0.63
	8.72^{x}		10.89^{x}		
aRaS	2.12	0.00	2.42	0.00	0.00
eReR	47.41^{x}	17.38	48.62^{x}	17.67	17.60
	18.87		17.04		
eReS	22.03	27.77	17.57	23.77	
eRaR	26.65^{x}	10.85	15.20	9.01	6.41
	8.56		6.05		
eRaS	14.36	13.40	11.90	11.07	8.12
	9.67^{x}		7.12^{x}		

*Zero points (kJ mol^{-1}): 44.369 (FF2'), 40.831 (FF2), 41.800 (FF3'a), 38.557 (FF3a), 891.093 (M6). R and S denote the absolute configuration of the N atom, *e* and *a* corresponds to equatorial and axial conformations, respectively, of the chelate ring with respect to the Bu^t group. The conformers with the water molecule situated on the Bu^t side of the molecule or *a*R chelate ring are marked with an *x*. The energy for eReS for M6 was impossible to obtain with the respective force field. For definition of force fields (FF2', M6 *etc.*) see Experimental.

both complex species irrespective of the force field or model used. After minimisation of the conformational potential other conformers yielded distinctly higher energies and very distorted coordination polyhedra.

Although having the comparable values for r.m.s. deviations with respect to valence angles and interatomic distances (Figure 2), we judge that the reproduction of the coordination polyhedron was not as successful as in the case of similar molecules, *bis*(*L-N,N*-dimethylisoleucinato)aquacopper(II)[9] and *bis*(*L-N,N*-diethyl-α-alaninato)aquacopper(II).[10] The most peculiar characteristic of the crystal structure is that the N–Cu–N* angle is changed more from its "ideal" value, *i.e.*, 180°, than the O1–Cu–O1* angle (Table III) which is virtually undistorted. Just the opposite is true for the theoretical structures (Table III, Figure 3), which consistently yielded higher distortion for the O–Cu–O angle than for the Nu–Cu–N angle*. By neglecting the apically bonded water molecule, even better results in term of r.m.s. deviation were obtained (Figure 3), which is contrary to experience with similar molecules.[9,10] To rule out the possibility of the inadequacy of our force fields, we systematically changed the most critical parameters for non-bonded interactions with OW, but no improvement was obtained.

All theoretical models equally well reproduced the overall geometry of the molecule. The r.m.s. deviation with respect to interatomic distances shows unusually narrow span (from 0.326 Å for FF3'a to 0.336 Å for FF1'). These values are also very high in comparison to similar molecules,[9,10] but the similarity of geometry between chelate rings (from 0.050 Å for FF1' to 0.059 Å for FF3'a) is close to the best reproduced crystal geometries.[13,14] That discrepancy can be obviously attributed to the

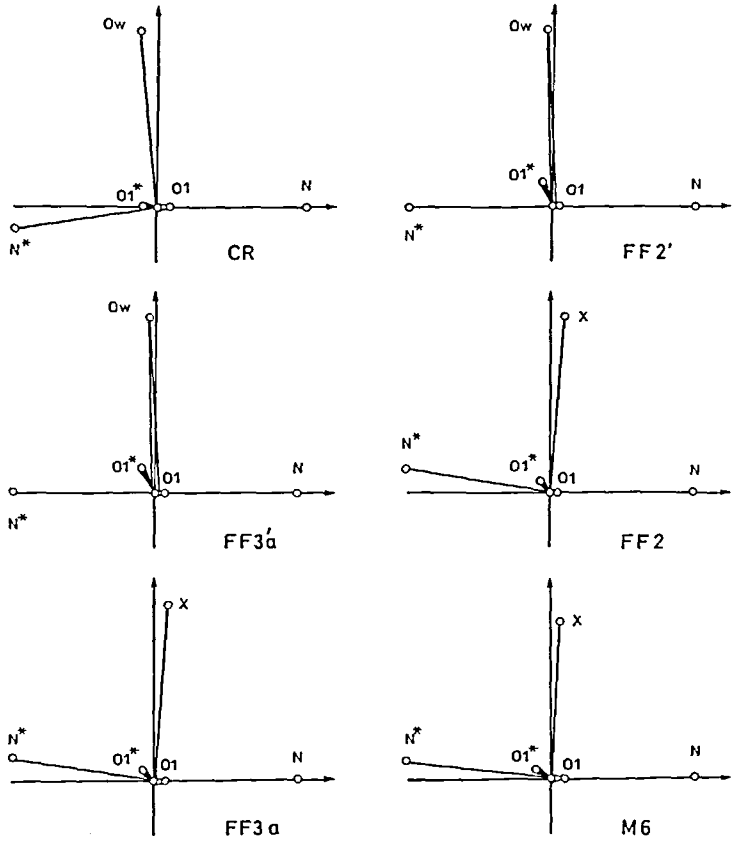

FIGURE 2 Comparison of X-ray and theoretical structures with respect to valence angles around copper expressed as $\varepsilon_{r.m.s.}(\Delta\theta)$. CR: coordination polyhedron in crystal; FF2, FF3'a, *etc.*: coordination geometry obtained with respective force fields (see Experimental). The mark 6 or 10 (*e.g.*, CR_6) denotes how many valence angles were taken into account. P1 denotes a square-planar structure and Py a square pyramid, the undistorted shapes of the coordination polyhedron.

imperfection in the reproduction of copper(II) coordination polyhedron. All theoretical structures are equally distorted from "ideal" (*i.e.*, planar and pyramidal) geometry (Figure 2) with the $\varepsilon_{r.m.s.}(\Delta\theta)$ values close to the value for the coordination polyhedron in the crystal structure. As expected, the "hard" force field FF1' yielded more planar structure than the other models, which was in accordance with experience with similar molecules.[7–10] Less expected was a structure obtained with theoretical model M5, which usually yields results close to those obtained with M6.[14]

Analysis of the similarity between crystal and theoretical structures strongly suggests that the distortion of the coordination polyhedron is determined mostly by intermolecular interactions (the other possibility, that discrepancy between theory and experiment is due to possible imperfections of molecular mechanics models or/and empirical parameters is less probable because all models yielded consistent results). In the molecule the bulky *tert*-butyl groups are axially disposed and there is no

TABLE III
Selected bond lengths (Å), valence and torsional angles (°) for *bis*(*N*-*tert*-Butyl-*N*-methylglycinato)aquacopper(II).

	Experimental	Theoretical (FF3'a)
Bond lengths		
Cu-N	2.081(2)	2.035
Cu-OW	2.464(2)	2.481
Cu-O1	1.922(2)	1.956
O1-C1	1.283(3)	1.281
O2-C1	1.221(3)	1.241
N-C2	1.488(3)	1.485
N-C3	1.476(3)	1.487
N-C4	1.528(3)	1.506
C1-C2	1.534(3)	1.516
C4-C5	1.531(4)	1.556
C4-C6	1.516(4)	1.552
C4-C7	1.526(4)	1.555
Bond angles		
N-Cu-N*	171.55(8)	179.37
O1-Cu-O1*	179.40(8)	169.67
OW-Cu-O1	89.70(6)	84.84
OW-Cu-N	94.23(5)	90.32
O1-Cu-N	84.85(7)	85.19
O1-Cu-N*	95.19(7)	94.86
Cu-O1-C1	114.4(1)	113.7
Cu-N-C2	100.5(1)	102.8
Cu-N-C3	109.2(1)	108.4
Cu-N-C4	114.7(1)	111.4
N-C2-C1	111.9(2)	110.3
N-C4-C5	111.9(2)	112.2
N-C4-C6	108.3(2)	110.3
N-C4-C7	110.4(2)	112.2
O1-C1-O2	125.2(2)	121.6
O1-C1-C2	115.7(2)	115.5
C2-N-C3	108.9(2)	108.5
C2-N-C4	112.6(2)	113.4
C3-N-C4	110.5(2)	111.9
O2-C1-C2	119.0(2)	122.9
C5-C4-C6	110.8(2)	108.0
C5-C4-C7	107.4(2)	107.1
C6-C4-C7	108.0(2)	106.9
Torsion angles		
N-Cu-O1-C1	−21.0(2)	−8.1
O1-Cu-N-C3	144.4(2)	139.6
Cu-O1-C1-C2	4.8(3)	−12.1
Cu-N-C2-C1	−34.8(2)	−36.4
Cu-N-C4-C5	−172.5(2)	−168.2
O1-C1-C2-N	23.1(3)	34.6

* Equivalent position $-x$, $-y$, z.

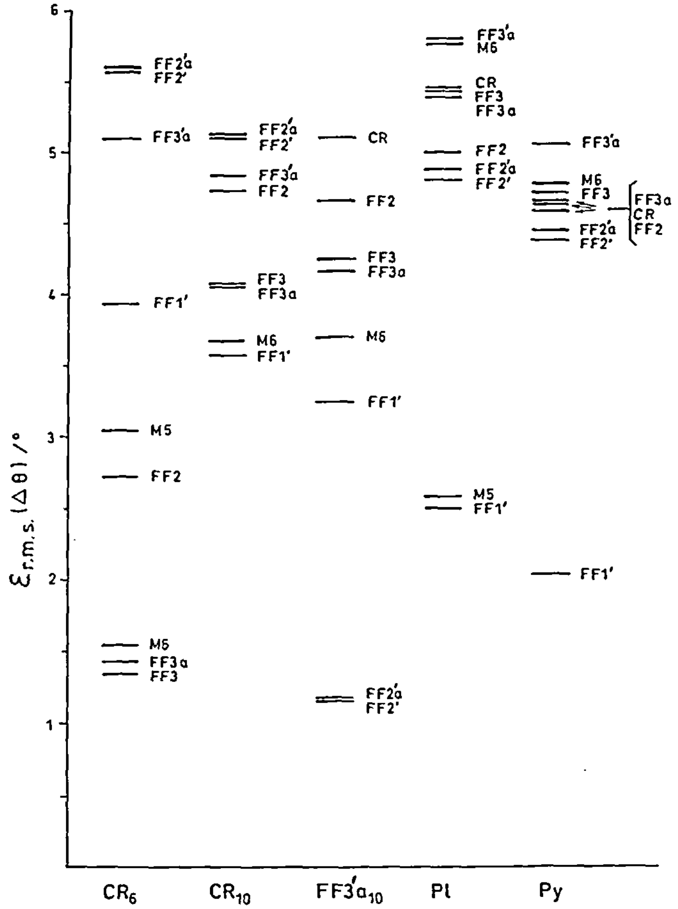

FIGURE 3 The shape of the coordination polyhedron of bis(N-*tert*-butyl-N-methylglycinato)-aquacopper(II) as observed in crystal structure (CR) and as obtained with divergent theoretical models (see Experimental). The structures with "dummy" atom X (having no non-bonded interactions with the rest of the molecule) are presented for comparison.

interaction between them [shortest *intra*molecular contact is C6···C6′ 4.426(5) Å]. The observed distortions of the copper coordination polyhedron in the crystal lattice may be attributable to packing effects; we note in this regard that the shortest *inter*molecular contact (apart from hydrogen bonding) is between the equatorial methyl group (C3) and the carbonyl oxygen (O2) of a neighbouring molecule which lies 3.451(4) Å above it. The direction of the observed N–Cu–N* angle bend is such as to accommodate the packing. For the detailed, *i.e.*, *quantitative*, analysis of that phenomenon more sophisticated theoretical models are needed. Development of such models will be the goal of further study.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid (to GF) and a visiting professorship (to BK) from the NSERC Canada, and Foundation for Scientific Research of Croatia (to NR). Thanks are due to Dr K. Rasmussen for allowing us to use his computer programs for molecular mechanics calculations.

REFERENCES

1. F. Basolo and Y.T. Chen, *J. Am. Chem. Soc.*, **76**, 953 (1954).
2. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **56**, 79 (1983).
3. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **57**, 1217 (1984).
4. V.A. Davankov, S.V. Rogozhin and A.A. Kurganov, *Iz. Akad. Nauk. SSSR, Ser. Khim.*, 204A, 000 (1971).
5. V.A. Davankov, S.V. Rogozhin and A.A. Kurganov and L.Ya. Zhuchkova, *J. Inorg. Nucl. Chem.*, **37**, 369 (1975).
6. V.A. Davankov and A.V. Semechkin, *J. Chromatogr.*, **141**, 313 (1977).
7. B. Kaitner, B. Kamenar, N. Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **15**, 373 (1987).
8. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **22**, 269 (1991).
9. B. Kamenar, M. Penavić, A. Škorić, N. Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **17**, 85 (1988).
10. G. Ferguson, B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, in press.
11. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **58**, 127 (1985).
12. J. Sabolović, N. Raos and K. Rasmussen, *Croat. Chem. Acta*, **62**, 495 (1989).
13. J. Sabolović and N. Raos, *Polyhedron*, **9**, 1277 (1990).
14. J. Sabolović and N. Raos, *Polyhedron*, **9**, 2419 (1990).
15. L.B. Kier and D. Dhawan, *J. Pharm. Sci.*, **51**, 1058 (1962).
16. R.E. Bowman and H.H. Stroud, *J. Chem. Soc.*, 1342 (1950).
17. P.C. Nash and W.P. Schaefer, *J. Amer. Chem. Soc.*, **91**, 1319 (1969).
18. B.A. Frenz and Associates Inc. (1983). *SDP-Plus Structure Determination Package*, College Station, Texas 77840, USA, and Enraf-Nonius, Delft, The Netherlands.
19. *International Tables for X-ray Crystallography* (1974), Vol. IV (Birmingham; Kynoch Press). Present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands.
20. N. Raos, S.R. Niketić and Vl. Simeon, *J. Inorg. Biochem.*, **16**, 1 (1982).
21. S.R. Niketić and K. Rasmussen, "The Consistent Force Field: A Documentation," (Springer-Verlag, Berlin, 1977); K. Rasmussen, "Potential Energy Functions in Conformational Analysis," (Springer-Verlag, Berlin, 1985).