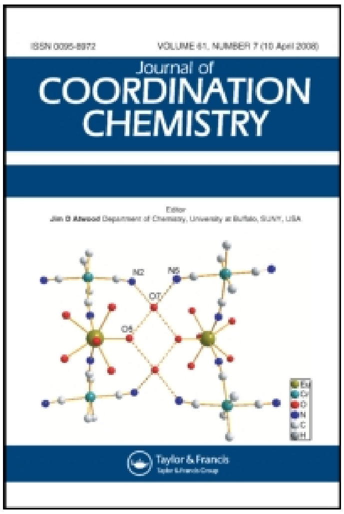

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Kaitner, B. , Ferguson, G. , Paulić, N. and Raos, N.(1993) 'STEREOCHEMISTRY OF COMPLEXES WITH N-ALKYLATED AMINO ACIDS. VII. CRYSTAL STRUCTURE OF BIS(N-tert-BUTYL-N-BENZYLGLYCINATO)COPPER(II). CONFORMATIONAL ANALYSIS AND MOLECULAR MECHANICS CALCULATIONS', Journal of Coordination Chemistry, 29: 4, 247 — 255

To link to this Article: DOI: 10.1080/00958979308037430

URL: http://dx.doi.org/10.1080/00958979308037430

J. Coord. Chem. 1993, Vol. 29, pp. 247–255
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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. VII. CRYSTAL STRUCTURE OF BIS(*N-tert*-BUTYL-*N*-BENZYLGLYCINATO)COPPER(II). CONFORMATIONAL ANALYSIS AND MOLECULAR MECHANICS CALCULATIONS

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(Received 29 September 1992)

The structure of the red, monoclinic modification of bis(*N-tert*-butyl-*N*-benzylglycynato)copper(II) was solved by X-ray diffraction analysis and refined to $R = 0.044$. The structure is made up of discrete molecules with the copper atom (situated at an inversion centre) having square-planar coordination with oxygen and nitrogen atoms in *trans* positions with Cu-O 187.4(2) and Cu-N 2.112(3)Å. The results of molecular mechanics calculations reveal that the crystal conformation has about 13 kJ mol^{-1} *higher* energy than the lowest energy conformation. This suggests the influence of intra- and intermolecular interactions in defining the molecular conformation.

KEY WORDS: bis(*N-tert*-butyl-*N*-benzylglycynato)copper(II), X-ray structure, conformational analysis, molecular mechanics.

INTRODUCTION

Among the chelates of copper(II) with α-amino acids and their *N*-alkylated and *N*,*N*-dialkylated derivatives, only few are truly tetracoordinated, i.e., they do not display apical coordination (*via* side group on C$^{\alpha}$-tom, water molecule or carboxylic oxygen from a neighbouring molecule). If there are bulky groups bound to the C$^{\alpha}$-atom or to nitrogen, severe distortion of coordination polyhedron takes place.[1–7] Centrosymmetric molecules, however, usually conserve their strictly planar coordination even if very high steric strain is generated due to close approach of bulky groups.[8–10]

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The principal aim of our research is to develop a molecular mechanics model which should predict the most probable conformation of copper(II) bis-chelates and α-amino acids to be expected in the crystal state, reproduce the diastereoselectivity (enantioselectivity)* effect as observed in nonaqueous solution,[11] and reproduce as accurately as possible the exact geometry of the complex, especially the shape of copper(II) coordination polyhedron. For the latter purpose, two novel empirical models were proposed. The first of them is based on a new function for conformational potential dependent on distortion coordinates.[12-14]

The second model treats interactions in the first coordination sphere (among the four ligand atoms and two apically placed charges) as being purely electrostatic.[15] Both models proved adequate in reproducing the shape of the coordination polyhedron of copper(II) bis-chelates with α-amino acids[7,13,15] and the enantioselectivity effect in the copper(II)/*N*,*N*-dimethylvaline system.[7,15]

The title compound, bis(*N*-*tert*-butyl-*N*-benzylglycynato)copper(II), is designed to study the influence of bulky groups bound to nitrogen on molecular conformation. In the case of a similar compound, bis(*N*-*tert*-butyl-*N*-methylglycinato)aquacopper(II),[16] molecular mechanics calculations correctly predicted the conformation of the molecule as observed in the crystal lattice. Unfortunately, our calculations were not so successful in predicting the shape of the coordination polyhedron, which was explained in terms of the influence of intermolecular hydrogen bonding. In this paper we have chosen a sterically hindered molecule in order to study the influence of bulky groups on molecular conformation, as well as on crystal packing.

EXPERIMENTAL

The ligand, *N*-*tert*-butyl-*N*-benzylglycine, was prepared by reaction of *N*-*tert*-butylglycine (the preparation of this substance is described elsewhere)[17] with benzylchloride.[18] The oily product was extracted with $CHCl_3$, remaining benzylalcohol removed by distillation (49–52°, 10 Torr) and the residue (benzyl ester of *N*-*tert*-butyl-*N*-benzylglycine; yield 68%) was hydrolyzed in 20% KOH/propylenglycol solution. The salt was converted to the acid by addition of HAc to pH = 2, and this was extracted with chloroform which was dried over $MgSO_4$. After evaporation of chloroform (60°C), the final product was obtained in the form of a volatile oil (total yield 63%) which was characterized by mass spectroscopy and nitrogen analysis. The complex was prepared by reaction of copper(II) acetate monohydrate and the sodium salt of *N*-*tert*-butyl-*N*-benzylglycine in CH_2Cl_2 solution.[19]

Crystal structure determination

$C_{26}H_{36}CuN_2O_4$, $M_r = 504.13$, monoclinic, space group $P2_1/a$, $a = 7.862(2)$, $b = 16.654(3)$, $c = 10.104(2)$Å, $\beta = 112.52(2)°$, $V = 1222.1(5)$Å^3, $Z = 2$, $D_x = 1.37\ \mathrm{g\,cm^{-3}}$, $F(000) = 534$, $\lambda = 0.7093$Å, $\mu(\mathrm{MoK}\alpha) = 9.3\ \mathrm{cm^{-1}}$.

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* $\Delta G = -RT\ln(\beta_{MLL}/\beta_{MDL})$, where β is the cumulative stability constant of the corresponding bis-complex with natural (*L*) or enantiomeric (*D*) form of the amino acid.

A red prism-shaped crystal of dimensions 0.37 × 0.35 × 0.24 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer with MoKα radiation. Cell parameters were determined from the setting angles of 25 reflections in the range $5 < \theta < 17°$. A total of 5872 intensities were collected in the range $4 < 2\theta < 54°$ using the θ-2θ scan mode (*hkl* range of reflections −10 to 9, 0 to 21, 0 to 12), of which 2730 were unique ($R_{int} = 0.043$) and not systematically absent. The 1715 reflections with $I \geqslant 3\sigma(I)$ were considered observed and used in structure solution and refinement. Three standard reflections monitored periodically throughout the data collection showed no evidence of crystal decay. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the *DIFABS* program in *SDP-Plus*.[20,21] The space group was determined uniquely from systematic absences *h*0*l*: $h = 2n$ and 0*k*0: $k = 2n$. The structure was solved by means of the heavy-atom method. A difference Fourier synthesis based on the copper atom position revealed the position of all non-hydrogen atoms. The positions of the hydrogen atoms were calculated on geometrical grounds with C—H = 0.95Å. Full-matrix least-squares anisotropic refinement of positional and thermal parameters of non-hydrogen atoms only led to convergence with $R = 0.044$, $R_w = 0.056$ and $GOF = 1.83$ for 151 variables with $w = 1/(\sigma^2 F_o + 0.055 F_o^2)$. A final difference Fourier map showed no significant features ($\rho_{max,min} = \pm 0.67$eÅ^{-3}); largest $\Delta/\sigma = 0.069$. Atomic scattering factors were provided by *SDP-Plus*.[21] Calculations were carried out on *PDP*11/73 computer using *SDP-Plus* and on a *PC* 386 personal computer using *NRCVAX*.[21,22] Table 1 lists atomic coordinates and equivalent isotropic thermal parameters and Table 2 gives bond lengths, valence angles and selected torsion angles. Figure 1 is an *ORTEP*II[23] presentation of the molecule in a general orientation.

Table 1 Final positional parameters (× 10^4) and equivalent isotropic thermal coefficients B_{eq}(Å^2)

	x/a	*y/b*	*z/c*	B_{eq}*
Cu	0	0	0	2.22(1)
O1	2269(3)	535(2)	678(2)	2.68(5)
O2	3682(3)	1669(2)	1647(3)	4.08(7)
N1	−933(4)	962(2)	907(3)	2.05(6)
C1	2307(4)	1254(2)	1171(4)	2.46(8)
C2	468(5)	1589(2)	1046(4)	2.68(8)
C3	−937(5)	718(2)	2386(4)	2.83(8)
C4	−2148(8)	3(4)	2229(4)	7.3(1)
C5	−1626(6)	1391(3)	3070(4)	4.4(1)
C6	1018(7)	519(4)	3371(5)	7.5(1)
C7	−2834(5)	1281(2)	−24(4)	2.72(8)
C11	−3085(4)	1522(2)	−1527(4)	2.72(8)
C12	−2773(6)	2304(3)	−1845(4)	3.6(1)
C13	−3086(7)	2538(3)	−3235(5)	4.9(1)
C14	−3747(7)	1991(3)	−4319(4)	5.7(1)
C15	−4119(7)	1226(3)	−4050(5)	5.2(1)
C16	−3792(6)	988(3)	−2652(4)	3.8(1)

*Anisotropically refined atoms are given the form of the isotropic equivalent thermal parameter defined as $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + abcos\gamma B_{12} + accos\beta B_{13} + bccos\alpha B_{23}]$.

Table 2 Selected bond lengths (Å), valence and torsion angles (°) for bis(*N*-*tert*-butyl-*N*-benzylgly cinato)copper(II)

	Experimental*	Theoretical (M6)
Bond lengths		
Cu-O1	1.874(2)	1.999
Cu-N1	2.112(3)	2.087
O1-C1	1.293(4)	1.274
O2-C1	1.215(4)	1.241
N1-C2	1.484(5)	1.488
N1-C3	1.550(5)	1.511
N1-C7	1.525(4)	1.498
C1-C2	1.509(5)	1.513
C3-C4	1.494(7)	1.554
C3-C5	1.522(7)	1.557
C3-C6	1.514(5)	1.552
C7-C11	1.509(5)	1.536
C11-C12	1.386(6)	1.411
C11-C16	1.381(5)	1.407
C12-C13	1.385(7)	1.405
C13-C14	1.365(7)	1.404
C14-C15	1.357(8)	1.404
C15-C16	1.394(7)	1.406
Bond angles		
O1-Cu-N1	85.4(1)	85.6
O1-Cu-N1*	94.6(1)	94.4
Cu-O1-C1	117.4(2)	111.1
Cu-N1-C2	101.9(2)	102.3
Cu-N1-C3	110.4(2)	108.5
Cu-N1-C7	114.7(2)	112.3
C2-N1-C3	111.6(2)	112.5
C2-N1-C7	109.3(3)	109.9
C3-N1-C7	108.8(3)	111.0
O1-C1-O2	124.3(4)	119.6
O1-C1-C2	115.4(3)	119.2
O2-C1-C2	120.1(3)	121.3
N1-C2-C1	113.6(3)	110.7
N1-C3-C4	110.1(3)	110.5
N1-C3-C5	112.2(3)	112.5
N1-C3-C6	108.4(4)	112.7
C4-C3-C5	108.2(4)	107.4
C4-C3-C6	109.9(4)	106.6
C5-C3-C6	108.1(3)	106.9
N1-C7-C11	115.7(3)	115.6
C7-C11-C12	121.1(3)	120.8
C7-C11-C16	120.9(4)	120.9
C12-C11-C16	117.7(4)	118.1
C11-C12-C13	121.4(4)	120.8
C12-C13-C14	119.5(5)	119.9
C13-C14-C15	120.7(4)	119.6
C14-C15-C16	120.0(4)	120.0
C11-C16-C15	120.7(4)	120.7
Torsion angles		
O1-Cu-N1-C3	−99.4(2)	−96.8
N1-Cu-O1-C1	−9.6(2)	−5.8
Cu-O1-C1-C2	−3.7(4)	−13.9
Cu-N1-C2-C1	−25.7(3)	−33.6

Table 2 *continued*

	Experimental*	Theoretical (M6)
O1-C1-C2-N1	22.0(4)	34.8
Cu-N1-C3-C4	−58.7(4)	−48.0
Cu-N1-C7-C11	−53.9(4)	−55.1
N1-C7-C11-C12	−92.1(5)	−87.2
C7-C11-C12-C13	−176.9(4)	173.8
C7-C11-C16-C15	176.4(4)	−174.1
C11-C12-C13-C14	1.2(8)	4.5
C12-C13-C14-C15	0.7(8)	2.3
C13-C14-C15-C16	−1.2(8)	−2.6
C14-C15-C16-C11	−0.2(8)	−3.9

*Symmetry code: −*x*, −*y*, −*z*.

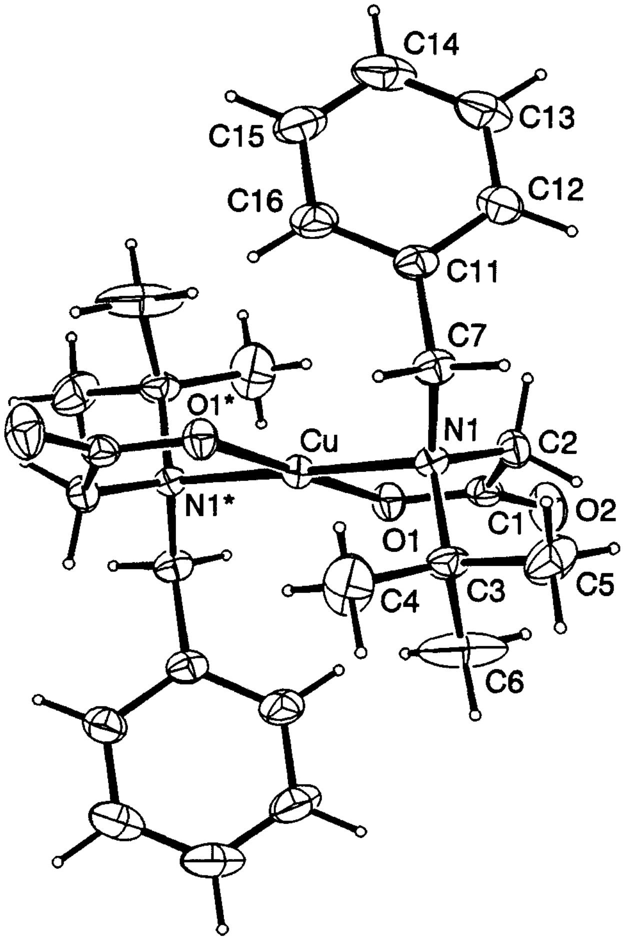

Figure 1 An *ORTEP*II drawing of the molecule showing the numbering system. Thermal ellipsoids are shown at the 35% probability level. The hydrogen atoms are shown as spheres of arbitrary radius.

Conformational analysis

The conformational potential was calculated from the basic formula (1)

$$\phi_T = \tfrac{1}{2}\sum_i k_{d,i}(d_i - d_{i,o})^2 + \tfrac{1}{2}\sum_j k_{\theta,j}(\theta_j - \theta_{o,j})^2 + \tfrac{1}{2}\sum_k \phi_n(1 \pm \cos n\gamma_k) + \sum_l (A_l \exp(-B_l r_l) - C_l r_l^{-6}) + \tfrac{1}{2}\sum_m k_{\chi,m}\chi_m^2 + \tfrac{1}{2}k_\beta(\beta - \beta_o)^2 + \phi_{cis} + \phi_{trans} + \phi_{el} \tag{1}$$

where d, θ, γ and χ stand for bond lengths, valence, torsional and out of plane angles, respectively; r is a non-bonded distance. K_d is an empirical parameter for bond stretching and k_θ for valence angle bending. Torsional interactions were determined with parameters ϕ_n and n (height and multiplicity of torsional barrier, respectively) and non-bonded interactions were computed from a Buckingham function with parameters A, B and C. In addition, the out-of-plane deformation potential for carboxyl groups and benzene ring with a quadratic function dependent on parameter k_χ was also taken into account.

The last four terms in equation (1) correspond to interactions specific for the copper coordination polyhedron. We altogether have proposed three kinds of models. They are a "dummy" atom model (FF1-FF3a),[24,25] a model with a distortion potential (M3-M5)[12-14] and an electrostatic model (M6).[15] The quadratic potential dependent on distortion coordinate β and parameters β_o and k_β is specific for force field 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 a cosine power series (M4, M5); ϕ_{el} is the coulombic potential between the charges situated around the copper atom (M6). A short overlay of models and parameters was given elsewhere.[7] Calculations were performed with a program developed by K. Rasmussen and coworkers.[26]

Similarity between the structures was expressed by the root-mean-square deviation (2)

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

where X stands for valence angles, θ, 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 structure contains discrete molecules separated by normal van der Waals interactions. The molecule lies in the 2(*a*) special position of the space group with the copper atom on a centre of inversion. The copper atom has the expected irregular square-planar coordination, with oxygen and nitrogen atoms in *trans* positions, with Cu-O and Cu-N bond distances 1.874(2) and 2.112(3)Å, respectively. The O-Cu-N angles (85.4(1) and 94.6(1)°) are significantly different from regularity. The C—N—C angles range from 101.9 to 114.7° with an average value of 109.5°. The average benzene

C—C distance is 1.378(7)Å. There are no unusual *intra*molecular bond distances and angles. The crystal geometry was fairly well reproduced with molecular mechanics calculations. Best results were obtained with the electrostatic model (M6) which yielded $\varepsilon_{\mathrm{r.m.s.}}(\Delta r) = 0.175$Å, and reproduction of angles around the copper atom within limits of experimental error (other force fields yielded $\varepsilon_{\mathrm{r.m.s.}}(\Delta r)$ values ranging from

Table 3 Minima of conformational energy for the chelate ring of bis(*N*-*tert*-butyl-*N*-benzylglycinato)copper(II)*

No.	Ring conformation	γ_1(°)	γ_2(°)	ϕ_T(kJ mol^{-1})
1	Bz(e)	−49.53	−98.55	30.85
2	Bz(e)	−40.04	−21.07	42.86
3	Bz(e)	63.57	−67.56	38.71
4	Bz(e)	177.42	−118.58	36.62
5	Bz(a)	60.50	116.02	40.35
6	Bz(a)	−62.81	84.82	24.89
7	Bz(a)	−174.90	79.73	37.92

*Calculations were carried out with force field FF3a. Torsion angles γ_1 and γ_2 correspond to angles Cu-N1-C7-C11 and N1-C7-C11-C12, respectively.

Table 4 Minima of conformation energy for bis(*N*-*tert*-butyl-*N*-benzylglycinato)copper(II)*

	FF3a		M6	
Conformation	*R,R*	*R,S*	*R,R*	*R,S*
1 1	0.00	13.05	0.00	13.33
1 2		10.67		9.62
1 3	20.70	36.24	19.25	35.44
1 4	14.06	15.69	13.65	15.53
1 5	14.64	14.70	13.39	13.68
1 6		1.80		1.64
1 7	24.82	19.10	23.17	18.57
2 3		30.99		28.96
2 4	12.39	10.68	12.56	10.13
2 5		30.60		27.09
2 7	19.79	22.72	18.22	20.33
3 3	46.90		44.13	63.55
3 4		41.62		40.50
4 4	24.35	22.81	10.13	22.35
4 5	24.50	25.83	23.31	24.61
4 6	13.38	12.61	13.07	12.06
4 7	35.00	32.41	33.27	31.32
5 5		35.68		32.59
5 7	23.31	36.06	22.62	32.53
6 6		26.35		23.51
6 7	10.88	24.01	11.30	20.47
7 7	29.11	46.18	29.00	40.39

*All energy values are expressed in kJ mol^{-1} with respect to the lowest conformer ($\phi_0 = 53.883$ kJ mol^{-1} (FF3a), $\phi_0 = 903.656$ kJ mol^{-1} (M6). Only conformers with relative conformation energy less than 50 kJ mol^{-1} were considered. For definition of force fields (FF3a and M6) see Experimental.

0.185 (FF3) to 197Å (FF3a) and $\varepsilon_{r.m.s.}(\Delta\theta)$ from 1.32 (FF3) to 2.38° (FF2)). The results obtained with force field M6 are comparable with reproduction of crystal geometry of similar molecules.[15]

Given that the chelate ring can adopt two conformations (axial and equatorial positions of the benzyl group) and three conformations of the benzyl group (torsion angle Cu-N1-C7-C11), at least six conformations of the chelate ring of bis(*N*-*tert*-butyl-*N*-benzylglycynato)copper(II) can be proposed. By a systematic search of conformational space, however, seven conformers were obtained (Table 3), due to two possible orientations of the benzene ring in the (Bz(e), $\gamma_1 \sim -60°$) conformer. It is of interest to note that the ring conformation observed in the crystal (1, Table 3) is not the most stable conformation; its energy is 5.96 kJ mol^{-1} *higher* than the energy of axial conformer 6.

By combination of ring conformations, it is possible to propose $7(7+1)/2=28$ conformations for the *R*,*R* and the same number of conformations for the *R*,*S* isomer. Due to very high interangular strain in most conformations, after minimization of conformational energy, only 36 conformations with acceptability low energy (i.e., 50 kJ mol^{-1} over the global minimum) were obtained (Table 4). Surprisingly, the conformation observed in the crystal state (1-1*R*,*S*) appears not to be the most stable; there are four *R*,*S* and three *R*,*R* conformers with lower strain energy. Essentially the same result was obtained with two quite different force fields (FF3a and M6). The fact that the crystal conformation does not correspond to the global minimum is not altogether surprising. All force fields gave consistent results yielding energy differences between 1-1*R*,*R* and 1-1*R*,*S* isomers ranging from 11.28 kJ mol^{-1} (FF1) to 13.72 kJ mol^{-1} (FF3). Moreover, in closely related systems with the same force fields, molecular mechanics calculations correctly predicted the crystal conformation.[6,7,10,16] Presumably, *inter*-molecular packing effects favour the conformation found in the crystal in this case.

Acknowledgements

This reseaarch was sponsored by the NSERC Canada with financial support through the award of an Operating Grant (to G.F.) and a visiting professorship (to B.K.). Thanks are aso due to Professor K. Rasmussen who kindly supported us with the program for conformational analysis and the Croatian Ministry for Science, Technology and Information.

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