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### STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALYKLATED AMINO ACIDS. I. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF *bis*-(*L*-*N*, *N*-DIMETHYLVALINATO)COPPER(II)

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# STEREOCHEMISTRY OF COMPLEXES WITH N-ALYKLATED AMINO ACIDS. I. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF *bis*-(L-*N,N*-DIMETHYLVALINATO)COPPER(II)

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The crystal structure of the red (orthorhombic, space group  $P2_12_12_1$ ) modification of *bis*-(L-*N,N*-dimethylvalinato) copper(II) was solved by X-ray diffraction and refined to  $R = 0.031$ . The coordination around the copper atom is of a tetrahedrally distorted planar nature, with N-Cu-O angles varying from 84.3° to 97.2°. The Cu-O bonds (1.896 and 1.902 Å) are considerably shorter and Cu-N bonds (2.022 and 2.026 Å) somewhat longer than those found in the majority of copper(II) amino acid chelate complexes.

The experimentally determined molecular structure was compared to that predicted theoretically, by using an empirical force-field method of conformational analysis. The theoretical method correctly reproduced the conformations of the chelate rings; molecular conformations found in the crystal were identical to the most stable conformations obtained theoretically. However, the force field used was not as successful in predicting the shape of the coordination polyhedron.

**Key words:** Copper, *bis*-(L-*N,N*-dimethylvalinato)copper(II), *N,N*-dimethylvaline, structure, conformation, empirical force-fields

## INTRODUCTION

Thermodynamic stereoselectivity in coordination complexes is closely connected with the plasticity of the coordination polyhedron of the central atom, *i.e.*, with the variability of the spatial arrangement of ligands around it. It has been noticed that the diastereoselectivity effect<sup>†</sup> is more pronounced for complexes with rigid geometry. Therefore, zinc and copper complexes with amino acids show a smaller difference in stability constants between the diastereomers<sup>1</sup> than do complexes of cobalt and nickel.

In previous papers<sup>2,3,4</sup> we suggested that, due to interannular repulsion between side chains of MLL isomer of copper(II) chelates with *N,N*-dimethylamino acids (valine or isoleucine), a deviation from the "ideal" planar geometry of the coordination polyhedron takes place; this deviation is absent in the sterically less hindered MDL isomer. In our first model (force field FF1)<sup>2,3</sup> we assumed a strictly planar coordination for copper which resulted in too high a value for the diastereoselectivity effect ( $\approx 9 \text{ kJ mol}^{-1}$ , compared with the experimental value<sup>5</sup> of  $3.5 \text{ kJ mol}^{-1}$ ). In order to obtain a better agreement between theory and experiment, we had tried to "hand-fit" the parameters in our empirical energy functions until we were able to reproduce reasonably well the crystal structures of *N*-allylated copper(II) salicylaldiminates.<sup>4</sup> The derived parameters (force fields FF2 and FF3, Table I) were not only satisfactory in reproducing the coordination polyhedron of some complexes of intermediate (planar/tetrahedral) geometry, but also reproduced the diastereoselectivity effect in *bis*-(*N,N*-

<sup>†</sup> Defined as  $-RT \ln(\beta_{MLL}/\beta_{MDL})$ , L and D denoting ligand enantiomers and  $\beta$  cumulative stability constants.

TABLE I  
 Parameters for force-field calculations

Internal coordinate	Empirical parameters <sup>†</sup> $k_{\theta}, k_{\nu}$ (kcal mol <sup>-1</sup> rad <sup>-2</sup> )			
	FF1	FF2	FF3	FF3a
N-Cu-O	97.784	97.784	11.0	11.0
X-Cu-O	97.784	9.0	11.0	11.0
X-Cu-N	97.784	9.0	11.0	11.0
$\lambda$	—	—	—	100.0

<sup>†</sup>FF1, force field from Ref. 2; FF2, FF3 - asymmetrical and symmetrical force fields, respectively, taken from Ref. 4; FF3a, improved FF3 (see Discussion); X, apically coordinated "dummy" atom. For all force fields  $\theta_0 = \pi/2$ .

dimethylvalinato)copper(II) complexes almost within the limits of experimental error.

The main aim of the present work was to see how closely an experimentally determined molecular geometry could be approximated by our empirical force-field models. For this purpose, it was necessary to determine the crystal structure of one of the compounds whose conformational properties had been studied, *i.e.*, *bis*-(L-*N,N*-dimethylvalinato)copper(II). The experimental crystal data can give reliable answers to several important questions, such as, does the coordination deviate from planarity, in which way and to what extent and, also, is the "most stable" (according to our calculations) conformer the one which is actually present in the solid state? Further, we wanted to obtain good experimental data in order to improve our conformational calculations on copper complexes or, more generally, to derive such a set of empirical functions for conformational potential which would be able to reproduce the geometries and energies of complexes with intermediate geometry. This aim, to reproduce as many properties of different molecules as possible with the same set of empirical functions, is an ultimate goal of the consistent force-field method,<sup>6</sup> which we have been trying to apply to copper aminoacidates.<sup>2-4,7,8</sup>

## EXPERIMENTAL

The ligand, L-*N,N*-dimethylvaline, was prepared by Bowman's method,<sup>9</sup> by methylation of L-valine through condensation with formaldehyde, followed by hydrogenation. The complex was prepared by means of reaction of copper(II) acetate monohydrate with the sodium salt of the ligand in dichloroethane solution.<sup>10</sup> On slow evaporation, blue-violet crystals were obtained but they gradually changed their colour to red; this phase transformation was accelerated by heating to 105°C. The crystals of the red modification suitable for X-ray analysis were obtained by crystallization from benzene solution. Unfortunately, the crystals of the blue modification were not suitable for X-ray structure analysis.

The colour difference between two phases is due to the apical ligation of carbonyl oxygens in the polymeric ( $[ML_2]_n$  blue modification).<sup>11</sup> Therefore, one should expect the red modification to crystallize from those solvents where the solubility of  $ML_2$  complex is too low to enable polymerization.

## Crystal structure analysis

$C_{14}H_{28}CuN_2O_4$ ,  $M = 351.9$ , orthorhombic, space group  $P2_12_12_1$ ,  $a = 6.698(4)$ ,  $b = 21.631(10)$ ,  $c = 12.011(9)$  Å,  $V = 1740.2$  Å<sup>3</sup>,  $D_c = 1.343$  g·cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 748$ ,  $\mu(\text{MoK}\alpha) = 12.12$  cm<sup>-1</sup>.

A prismatic crystal of dimensions  $0.27 \times 0.26 \times 0.43$  mm was used for data collection. The experimental data were collected on a Philips PW1100 four-circle diffractometer using MoK $\alpha$  radiation. Unit cell parameters were obtained by a least-squares refinement of 18 angular settings. Intensities were collected up to  $\theta = 30^\circ$  ( $h$  0–9;  $k$  0–30;  $l$  0–16) by the  $\mu$ - $2\theta$  scan mode. Three standard reflections were monitored every two hours and showed no significant change. Of the 2479 independent reflections, 2327 with  $I \geq 3\sigma(I)$  were used in the crystal structure determination. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved using Patterson and Fourier syntheses and refined by least-squares method assuming anisotropic thermal motion for all non-hydrogen atoms. Hydrogen atom positions were derived either from known geometry or from a difference Fourier synthesis. They were included in the calculations but were not refined. The refinement converged at the final  $R = 0.031$  ( $R_w = 0.035$ ). The function minimised was  $\Sigma w(|F_o| - |F_c|)^2$  with  $w = 1.0739/\sigma^2(F_o) + 0.000885F_o^2$ . A final difference Fourier map showed no significant residues. The anomalous dispersion correction was included in the  $F_c$  calculations with the atomic scattering factors taken from International Tables for X-ray Crystallography.<sup>12</sup> Final atomic coordinates and  $U_{eq}$  values are listed in Table II.

Atomic coordinates of the hydrogen atoms, atomic thermal parameters and the list of calculated and observed structure factors are available on request from the authors. All calculations were carried out on the UNIVAC 1110 computer of the University Computing Centre in Zagreb and mostly were performed with SHELX76.<sup>13</sup>

TABLE II

Final fractional atomic coordinates ( $\times 10^4$ , for Cu  $\times 10^5$ ) with e.s.d.'s in parentheses for non-H atoms and  $U_{eq}$  ( $\times 10^4$ )<sup>a</sup>.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (Å <sup>2</sup> )
Cu	15870(5)	15968(2)	18983(3)	318(1)
O(11)	-368(3)	1699(1)	772(2)	396(6)
O(12)	-946(4)	1572(1)	-1030(2)	615(8)
N(1)	3357(4)	1313(1)	635(2)	330(6)
C(11)	64(5)	1492(1)	-204(3)	383(8)
C(12)	2006(4)	1114(1)	-291(2)	345(8)
C(13)	1558(6)	416(1)	-315(3)	443(9)
C(14)	503(8)	242(2)	-1411(4)	695(16)
C(15)	359(7)	190(2)	682(4)	588(14)
C(16)	4974(5)	873(2)	896(3)	484(12)
C(17)	4291(6)	1909(2)	310(3)	500(11)
O(21)	3482(3)	1432(1)	3040(2)	437(7)
O(22)	4064(4)	1582(2)	4833(2)	661(11)
N(2)	278(4)	2141(1)	3062(2)	350(7)
C(21)	2984(4)	1612(2)	4033(2)	401(8)
C(22)	822(5)	1865(2)	4150(2)	359(8)
C(23)	-605(5)	1341(2)	4530(3)	452(10)
C(24)	-29(7)	1104(2)	5694(3)	639(14)
C(25)	-731(6)	800(2)	3705(3)	582(13)
C(26)	-1886(5)	2282(2)	2944(3)	465(10)
C(27)	1401(6)	2734(2)	2940(3)	507(10)

<sup>a</sup> $U_{eq} = (4/3) \Sigma \Sigma U_{ij} a_i a_j$  (see ref.<sup>13</sup>).

*Conformational analysis*

The theoretical conformational analysis was based upon the minimisation of the conformational (strain) potential energy, calculated from the empirical formula (1).

$$V = \frac{1}{2} \sum_i k_{b,i} (b_i - b_{0,i})^2 + \frac{1}{2} \sum_j k_{\theta,j} (\theta_j - \theta_{0,j})^2 + \frac{1}{2} \sum_k V_{n,k} (1 \pm \cos n\phi) + \frac{1}{2} \sum_l k_{\chi,l} \chi_l^2 + \sum_m A_m \exp(-B_m r_m) - C_m r_m^{-6} \quad (1)$$

in which  $b$ ,  $\theta$ , and  $\phi$  stand for bond lengths, valence and torsional angles, respectively,  $r$  is non-bonded distance;  $k_b$  is an empirical parameter for bond stretching and  $k_\theta$  for valence angle bending. Torsional interactions were determined with parameters  $V_n$  and  $n$ , and non-bonded interactions were computed from a Buckingham function with parameters  $A$ ,  $B$  and  $C$ . In addition, in one of the force fields (FF3a, Table I) the out-of-plane torsional potential for the carboxyl group was also computed by using the function with an empirical parameter,  $K_\chi$ , and the out-of-plane torsion angle,  $\chi$ . The parameters were the same as used in our first paper<sup>7</sup> with the exception of C-N-C bending parameters which were taken to be equal to the parameters for C-C-C bending. The parameters for valence angle bending around the copper atom depend on the force field used (Table I). Calculations were performed with the program developed by Niketić and Rasmussen.<sup>14</sup>

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

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

where  $X$  stands for either the valence angles ( $\theta$ ) or interatomic distances ( $r$ ) while  $\Delta$  denotes the difference between the observed and the calculated value of the observable  $X$ .

**RESULTS AND DISCUSSION**

Interatomic distances and angles as well as selected torsion angles are given in Table III, while Figure 1 shows a perspective diagram of the complex molecule with the atom numbering scheme.

The structure consists of independent molecules held together by van der Waals interactions. There are no intermolecular contacts closer than 3.267 Å. Bond lengths and angles within the ligands are normal and in good agreement with values found in related structures. The complex has a *trans*-structure, similar to those found in other *bis*(aminoacidato)copper(II) complexes.<sup>10,15,16</sup> The copper atom has a distorted planar coordination with N-Cu-O angles ranging from 84.3(1) to 97.2(1)°. The deviations from planarity, *i.e.* from the least-squares best plane through the copper, two nitrogen and two oxygen atoms, are Cu -0.10, N(1) 0.23, N(2) 0.22, O(11) -0.17, and O(21) -0.18 Å, so that the coordination polyhedron is best described as a very flattened tetrahedron. The Cu-N bonds of 2.022(2) and 2.026(3) Å are somewhat longer, and the Cu-O bonds of

TABLE III  
Interatomic distances/Å, angles/° and selected torsion angles†/°.

Ring(1)	Ring(2)		Difference Ring(1)-Ring(2)	Theoretical value <sup>††</sup>	Difference Exp. -theor.
Cu-O(11)		1.896(2)			-0.065
	Cu-O(21)	1.902(2)	-0.006	1.961	-0.059
Cu-N(1)		2.022(2)			0.023
	Cu-N(2)	2.026(3)	-0.004	1.999	0.027
O(11)-C(11)		1.288(4)			-0.001
	O(21)-C(21)	1.298(4)	-0.010	1.289	0.009
O(12)-C(11)		1.213(4)			-0.028
	O(22)-C(21)	1.205(4)	0.008	1.241	-0.036
N(1)-C(12)		1.496(4)			0.010
	N(2)-C(22)	1.490(4)	0.006	1.486	0.004
N(1)-C(16)		1.476(4)			-0.007
	N(2)-C(26)	1.488(4)	-0.012	1.483	0.005
N(1)-C(17)		1.486(5)			0.004
	N(2)-C(27)	1.495(4)	-0.09	1.482	0.013
C(11)-C(12)		1.540(4)			0.016
	C(21)-C(22)	1.548(4)	-0.008	1.524	0.024
C(12)-C(13)		1.541(4)			-0.022
	C(22)-C(23)	1.537(5)	0.004	1.563	-0.026
C(13)-C(14)		1.540(6)			-0.009
	C(23)-C(24)	1.538(6)	0.002	1.549	-0.011
C(13)-C(15)		1.522(6)			-0.028
	C(23)-C(25)	1.534(6)	-0.012	1.550	-0.016
O(11)-Cu-N(1)		84.5(1)			0.8
	O(21)-Cu-N(2)	84.3(1)	0.2	83.7	0.6
Cu-O(11)-C(11)		117.0(2)			2.8
	Cu-O(21)-C(21)	115.8(2)	1.2	114.2	1.6
Cu-N(1)-C(12)		106.9(2)			0.2
	Cu-N(2)-C(22)	105.0(2)	1.9	106.7	-1.7
Cu-N(1)-C(16)		117.8(2)			4.5
	Cu-N(2)-C(26)	118.4(2)	-0.6	113.3	5.1
Cu-N(1)-C(17)		100.4(2)			-3.4
	Cu-N(2)-C(27)	102.3(2)	-1.9	103.8	-1.5
	O(11)-Cu-O(21)	175.7(1)		176.8	-1.1
	N(1)-Cu-O(21)	95.3(1)		95.8	-0.5
	O(11)-Cu-N(2)	97.2(1)		95.8	1.4
	N(1)-Cu-N(2)	161.5(1)		169.8	-8.3
C(12)-N(1)-C(16)		114.7(2)			1.0
	C(22)-N(2)-C(26)	113.9(2)	0.8	113.7	0.2
C(12)-N(1)-C(17)		108.0(2)			-2.1
	C(22)-N(2)-C(27)	108.5(2)	-0.5	110.1	-1.6
C(16)-N(1)-C(17)		107.9(3)			-1.0
	C(26)-N(2)-C(27)	107.7(3)	0.2	108.9	-1.2
O(11)-C(11)-O(12)		124.7(3)			3.3
	O(21)-C(21)-O(22)	124.2(3)	0.5	121.4	2.8
O(11)-C(11)-C(12)		115.9(3)			0.3
	O(21)-C(21)-C(22)	115.2(2)	0.7	115.6	-0.4
O(12)-C(11)-C(12)		119.4(3)			-3.6
	O(22)-C(21)-C(22)	120.5(3)	-1.1	123.0	-2.5

continued

Table III continued

Ring(1)	Ring(2)		Difference Ring(1)-Ring(2)	Theoretical value <sup>††</sup>	Difference Exp. -theor.
N(1)-C(12)-C(11)	108.9(2)		1.1	106.7	1.3
N(2)-C(22)-C(21)	106.9(2)				0.2
N(1)-C(12)-C(13)	114.4(2)		0.3	114.6	-0.2
N(2)-C(22)-C(23)	114.1(3)				-0.5
C(11)-C(12)-C(13)	111.0(3)		-0.2	109.4	1.6
C(21)-C(22)-C(23)	111.2(3)				1.8
C(12)-C(13)-C(14)	110.1(3)		-0.7	110.3	-0.2
C(22)-C(23)-C(24)	110.8(3)				0.5
C(12)-C(13)-C(15)	113.8(3)		0.6	112.8	1.0
C(22)-C(23)-C(25)	113.2(3)				0.4
C(14)-C(13)-C(15)	110.6(3)		0.3	108.9	1.7
C(24)-C(23)-C(25)	110.3(3)				1.4
Cu-O(11)-C(11)-C(12)	7.9(4)		0.5	14.9	-7.0
Cu-O(21)-C(21)-C(22)	7.4(4)				-7.5
Cu-N(1)-C(12)-C(11)	28.9(3)		-7.7	37.0	-8.1
Cu-N(2)-C(22)-C(21)	36.6(3)				-0.4
O(11)-C(11)-C(12)-N(1)	-25.4(4)		5.5	-35.4	10.0
O(21)-C(21)-C(22)-N(2)	-31.9(4)				4.5
O(11)-Cu-N(1)-C(12)	-21.2(2)		6.9	-30.9	9.7
O(21)-Cu-N(2)-C(22)	-28.1(2)				2.8
N(1)-Cu-O(11)-C(11)	8.1(3)		-4.1	6.2	1.9
N(2)-Cu-O(21)-C(21)	12.2(3)				6.0
O(11) ... C(17 <sup>i</sup> )	3.286				
O(12) ... C(17 <sup>i</sup> )	3.401				
O(12) ... C(27 <sup>i</sup> )	3.267				
C(11) ... C(17 <sup>i</sup> )	3.498				

<sup>†</sup> Estimated standard deviations are given in parentheses; symmetry transformation: (i)  $1/2+x, 1/2-y, -z$ .

<sup>††</sup> Theoretical structure: conformation obtained by minimization with FF3a.

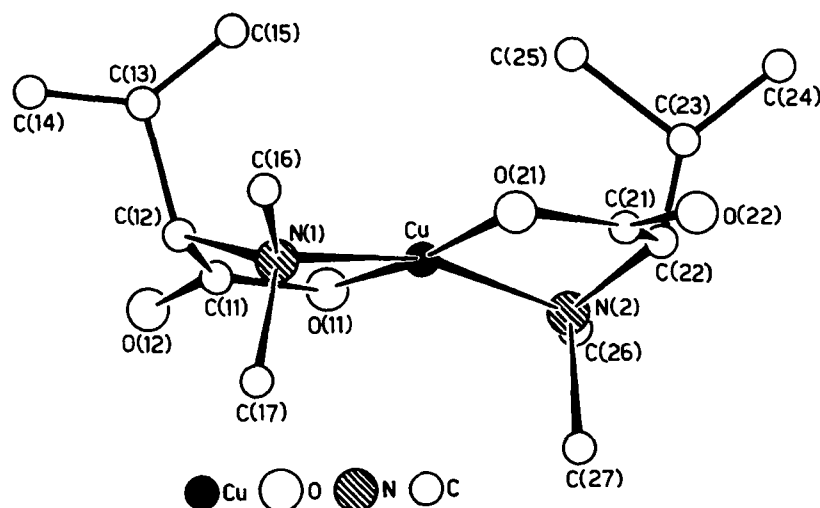


FIGURE 1 Molecular structure of *bis*-(*L*-*N,N*-dimethylvalinato)copper(II), showing the atom labelling scheme. Hydrogen atoms are omitted for clarity

1.896(2) and 1.902(2) Å significantly shorter than the values found for such bonds in the majority of amino acid complexes of copper(II).<sup>17</sup> However, there are examples with the analogously longer Cu-N and shorter Cu-O bond lengths, for instance in the structures of *bis*(L-alaninato)copper(II),<sup>18</sup> *bis*(L-asparaginato)copper(II),<sup>16</sup> *bis*(*N*-benzyl-L-valinato)copper(II),<sup>20</sup> and in *bis*(DL-*N,N*-diethyl- $\alpha$ -alaninato)copper(II).<sup>10</sup>

The molecular conformation found in the crystal structure, compared to the predicted one, shows a general agreement, *i.e.*, the actual conformation in the crystal structure corresponds to that predicted as the most stable (6-6 in our notation<sup>2</sup>) with any of the force fields examined. As expected on the grounds of both theoretical arguments and thermodynamic results (see Introduction), the coordination of copper is not planar.

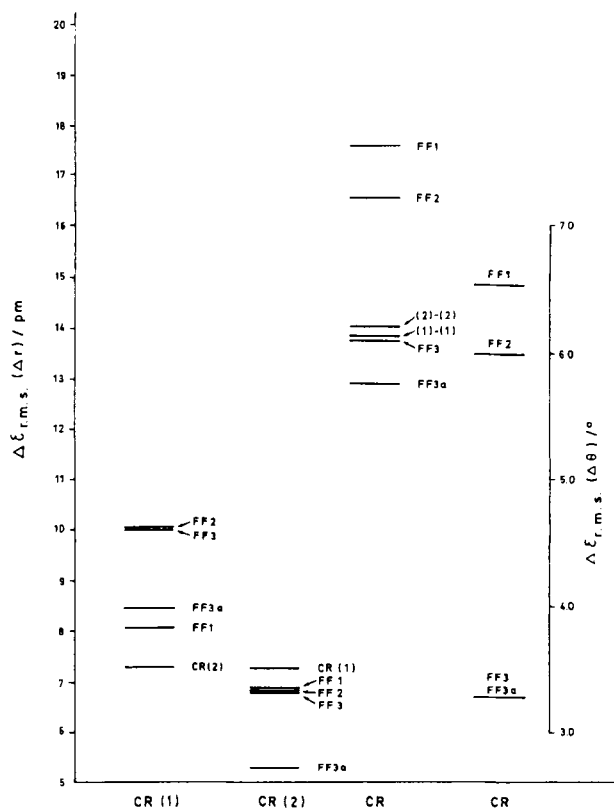


FIGURE 2 Comparison of X-ray molecular structure with theoretically predicted conformations. CR: molecular conformation in the crystal; (1)-(1) and (2)-(2): "constructed" crystal structures (see text); CR(1) and CR(2): chelate rings (1) and (2) having the conformation CR; FF1, FF2, etc.: conformations obtained with respective force fields (see Table I);  $\epsilon_{r.m.s.}(\Delta r)$  was computed by neglecting H atoms;  $\epsilon_{r.m.s.}(\Delta \theta)$  refers to six valence angles defining the geometry of copper coordination

The values of  $\epsilon_{r.m.s.}(\Delta r)$  for individual chelate rings (first two columns in Fig. 2) show that all force fields reproduce fairly closely (within  $ca \pm 0.07$  Å) the conformation of ring(2) in the crystal structure; for ring (1), however, the prediction is less accurate (within  $\pm 0.085$  Å). It should be noted that any of the theoretically predicted structures resembles more closely the actual conformation of ring (2) than the two chelate rings resemble each other. The lowest value for  $\epsilon_{r.m.s.}(\Delta r)$  was obtained with the force field FF3a, owing to the out-of-plane torsion potential introduced into this model.



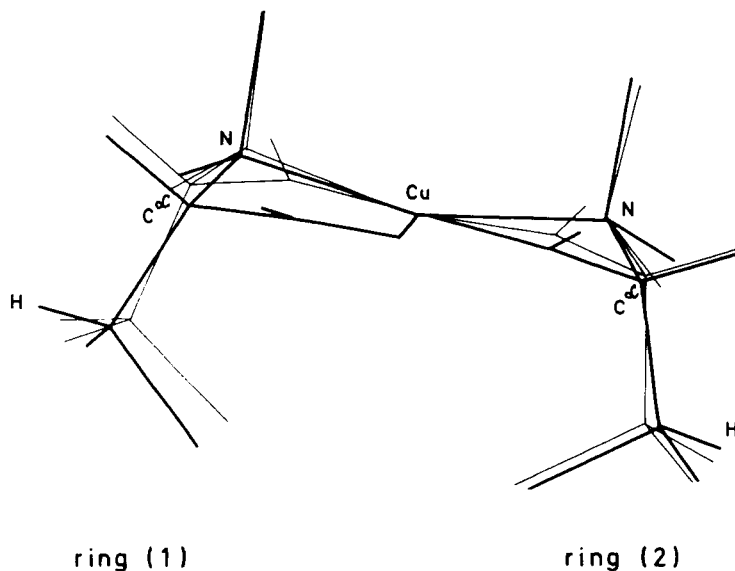


FIGURE 3 Comparison of X-ray and theoretically computed (force field FF3a) structures: heavy line: X-ray structure, thin line: theoretical structure

The same is seen when the observed and predicted distances are compared for the whole complex molecule (third column in Fig. 2 and, also, Fig. 3). The similarity between the predicted (FF3a) and the actual conformations is even greater than the resemblance of the latter to the artificially constructed (1)-(1) or (2)-(2) conformations obtained by combining the conformations of individual rings as found in the crystal.

The copper coordination polyhedron, a severely distorted tetrahedron in crystal structure, was not very well reproduced by our theoretical models. Again, the best agreement, judged from  $\epsilon_{r.m.s.}(\Delta\theta)$  for six relevant angles (O-Cu-O, N-Cu-N and O-Cu-N), was obtained with FF3a (fourth column in Fig. 2).

It can be concluded that the symmetrical force field with the additional potential for the out-of-plane torsion of the carboxylic group (FF3a) was the most successful in predicting the chelate ring conformation as well as the distortion of the coordination polyhedron. The comparison of structural parameters for the crystal with those predicted by using the force field FF3a is given in Table III.

Although the force field FF3a is, beyond any doubt, one of the best models devised so far for predicting the structural properties of copper(II) aminoacidates it failed to reproduce two structural features: the shape of the coordination polyhedron and the non-equivalence of the two chelate rings. Whether these specific structural features are to be explained by intermolecular interactions (packing forces were not taken into account in our calculations) or by assuming some additional intramolecular potentials remains an open question which would be difficult to answer on the basis of the available empirical data.

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