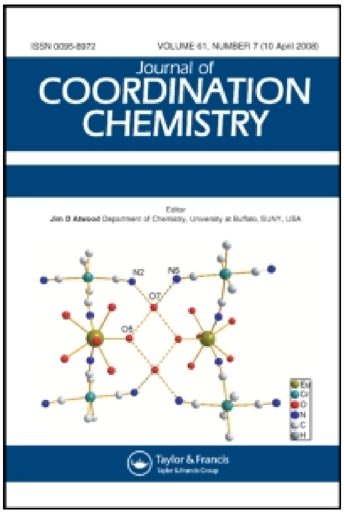

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STEREOCHEMISTRY OF COMPLEXES WITH *N*-ALKYLATED AMINO ACIDS. II. CRYSTAL STRUCTURE AND CONFORMATIONAL ANALYSIS OF *BIS*-(*L*-*N*,*N*-DIMETHYLISOLEUCINATO) AQUACOPPER(II)

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The crystal structure of blue, orthorhombic (space group $P2_12_12_1$) modification of *bis*-(*L*-*N*,*N*-dimethylisoleucinato)aquacopper(ii) was solved by X-ray diffraction and refined to $R = 0.047$. The coordination geometry around the copper atom is described by tetrahedrally distorted pyramid, with N–Cu–O angles varying from 83.4° to 97.6°. The variation in distance of Cu–O bonds (1.900 and 1.949 Å) is considerably greater than the same variation of Cu–N bonds (2.014 and 2.019 Å). The copper–oxygen distance (from ligated water) is 2.448 Å which is significantly longer than the Cu–O bonds in chelate rings.

The experimentally determined molecular structure was compared to several theoretically predicted ones by using an empirical force-field method of conformational analysis. Theoretical predictions fitted well the observed geometry of the coordination polyhedron only when non-bonding interactions with the apically ligated water molecule were taken into account.

Keywords: *N*,*N*-dimethylisoleucine, copper, complex, structure, conformation

INTRODUCTION

The study of copper(II) chelates with *N*-alkylated amino acids has two principal goals. First it is helpful in explaining the diastereoselective formation of these compounds[1] which have been thoroughly investigated as potentially suitable substances for separation of enantiomers of amino acids by ligand-exchange chromatography.[2] Second, a more fundamental goal is, taking these substances as model compounds, to derive an empirical force field suitable for the calculation of stereochemical and thermodynamic properties of copper(II) complexes with biologically significant ligands (*e.g.* amino acids and peptides). To achieve this it is of utmost importance to obtain such an empirical force field (*i.e.* an analytical expression for conformational potential and a set of empirical parameters) which would fairly well reproduce the most specific property of copper stereochemistry, its "plasticity".[3]

"Plasticity" of copper complexes, *i.e.* their tendency to build "distorted" coordination polyhedra, instead of "regular" coordinations (square-planar or tetrahedral) results in smaller diastereoselectivity effects in copper complexes compared to complexes of metals with more rigid geometry (*e.g.* cobalt or nickel).[4] The distorsion of the copper polyhedron also modifies the redox potential of copper-dependent enzymes, such as plastocyanins.[5] In previous papers we have tried to calculate the geometry and energy of copper chelates with dimethylated valine[6–8] and isoleucine.[9] If too "strong" a force field is used (FF1, Table I) the calculated diastereoselectivity effect is systematically higher than the measured one.[6,9] If angle bending parameters around copper are set to lower values (FF2 and FF3)[7] a better agreement with thermodynamic data was achieved, but unfortunately these force fields yielded the wrong coordination polyhedron, *viz*, a distorted pyramid instead of a distorted tetrahdron.[8]

In the first paper of this series[8] we were concerned with an anhydrous complex, *bis*-(*N*,*N*-dimethylvalinato)copper(II). Here we report the crystal structure and conformational properties of a cognate but structurally more complicated molecule, *bis*-(*N*,*N*-dimethylisoleucinato)copper(II) monohydrate. This compound contains an apically bound water molecule which could exert additional steric influences. First, it could determine the conformation of chelate rings by preventing the rings from assuming conformations with too close a contact between the amino acid side chain and the centre of the molecule (these conformations were shown to be most stable[9]). Secondly, it could influence the geometry of chelate rings and/or copper coordination polyhedron by intramolecular and intermolecular interactions. Explaining and possibly predicting these influences in a more or less quantitative way is the principal goal of the consistent force field (CFF) method[10] which we have been trying to apply in such complex compounds.

EXPERIMENTAL

The ligand, *L*-*N*,*N*-dimethylisoleucine, was prepared by Bowman's method,[11] by methylation of *L*-isoleucine through condensation with formaldehyde, followed by hydrogenation. The complex was prepared by reaction of copper(II) acetate monohydrate with the sodium salt of the ligand in CH_2Cl_2 solution, and it was recrystallized from benzene to obtain the blue modification. This crystal modification loses water about 87°C, with complete decomposition taking place at 147°C.

Crystal structure analysis

$Cu(C_8NO_2H_{16})_2.H_2O$. $M_r = 400.00$, orthorhombic, space group $P2_12_12_1$, $a = 22.154(5)$, $b = 15.032(4)$, $c = 6.032(3)$ Å, $V = 2008.8$ Å^3, $D_m = 1.260\ \mathrm{g\,cm^{-3}}$ (by flotation), $D_c = 1.262\ \mathrm{g\,cm^{-3}}$, $Z = 4$, $F(000) = 844$, $\mu(\mathrm{Cu}K\alpha) = 16.07\ \mathrm{cm^{-1}}$.

A prismatic crystal of dimensions $0.08 \times 0.03 \times 0.42$ mm was used for data collection on a Philips PW 1100 four-circle diffractometer (graphite monochromator, Cu$K\alpha$ radiation, $\omega - 2\theta$ technique); 18 reflections were used to determine cell parameters. Intensities were collected within the range $3 < \theta < 35°$ ($0 < h < 26$, $0 < k < 18$, $0 < l < 7$). Three standard reflections were monitored every two hours and showed no significant change with time. Of the 1707 independent reflections 1512 with $I > 3\sigma(I)$ were used in the crystal structure determination. 14 reflections were rejected because of too great a difference between F_o and F_c. Data were corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous dispersion correction for Cu atom were taken from International Tables for X-ray Crystallography.[13]

The structure was solved by means of Fourier syntheses based upon coppper atom coordinates obtained from a Patterson synthesis and refined by least-squares method assuming anisotropic thermal motion of all non-hydrogen atoms. Hydrogen atoms belonging to the water molecules were located in difference Fourier maps and refined with a fixed isotropic temperature factor $U_{iso} = 0.050$ Å^2. The positions of all other hydrogen atoms were derived geometrically and included in the structure calculation.

The refinement converged at the final $R = 0.047$ ($R_w = 0.056$). The function minimized was $\Sigma w(F_o - F_c)^2$ with $w = 1.000\,|\sigma F_o + 0.007492\,F_o^2|^{-1}$. A final difference Fourier map showed no significant residuals. Final atomic coordinates and U_{eq} values are listed in Table II.

Atomic coordinates of the hydrogen atoms, anisotropic thermal parameters and list of observed and calculated structure factors have been deposited with the Editor-in-Chief. All calculations were performed using a UNIVAC 1110 computer with the SHELX76 program.[14]

Conformational analysis

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

$$\begin{aligned} V = {} & \tfrac{1}{2}\sum_i k_{b,i}(b_i - b_{0,i})^2 + \tfrac{1}{2}\sum_j k_{\theta,j}(\theta_j - \theta_{0,j})^2 \\ & + \tfrac{1}{2}\sum_k V_{n,k}(1 \pm \cos n\varphi_k) + \tfrac{1}{2}\sum_l k_{\chi,l}\,\chi^2 \qquad (1) \\ & + \sum_m A_m \exp(-B_m r_m) - C_m r_m{}^{-6} \end{aligned}$$

In this equation b, θ and φ 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_θ 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 two of the force fields (FF2 and 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_χ, and the out-of-plane torsion angle, χ. The parameters were the same as those used in our previous paper,[12] 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.[10] All of the molecules were computed with two apically bound "dummy" atoms, *i.e.*, as octahedral complexes.

Root-mean-square deviatons were calculated from the formula

$$\varepsilon_{\text{r.m.s.}}(\Delta X) = \tfrac{1}{2}\sum_{i=1}(\Delta X_i)^2$$

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

RESULTS AND DISCUSSION

The copper atom of the title complex has a square pyramidal coordination; the basal plane is occupied by two nitrogen and two oxygen atoms from two dimethylisoleucinato ligands while the fifth apical site is occupied by a water oxygen atom (Fig. 1). The Cu–N bond lengths of 2.014(5) and 2.019(5) Å, and the Cu–O bonds (to the amino acid) of 1.900(5) and 1.949(5) Å, respectively, are similar to values found in the corresponding *bis*-(*L*-*N*,*N*-dimethylvalinato)copper(II) complex.[8] The copper to oxygen distance (water molecule) is significantly longer (2.448(6) Å).

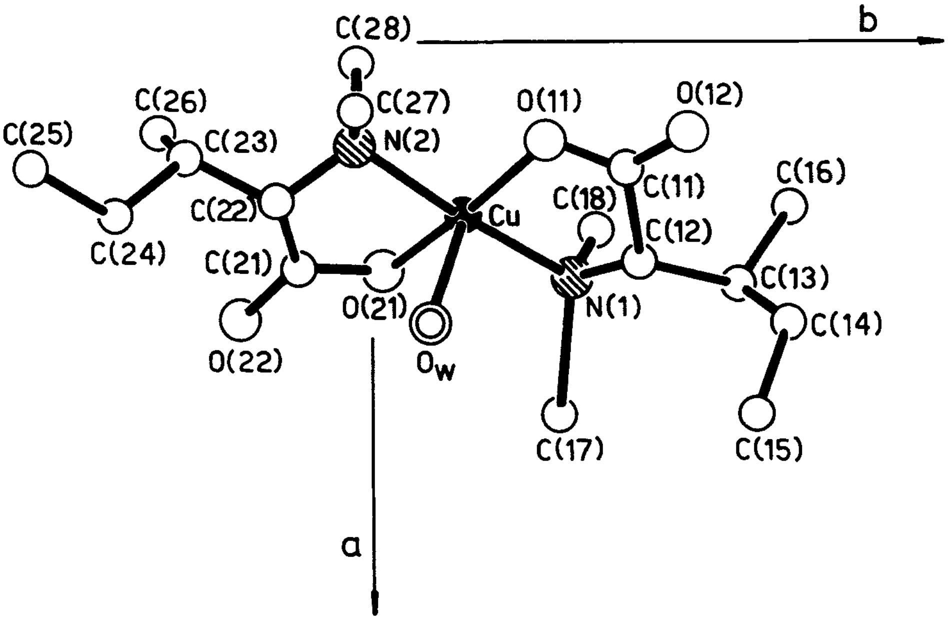

FIGURE 1 Molecular structure of *bis*-(*L*-*N*,*N*-dimethyl-isoleucinato)aquacopper(II). Hydrogen atoms are omitted for clarity.

The basal plane shows little deviation from planarity. Two oxygen atoms, O(11) and O(21) are above (0.0543 and 0.0534 Å) while the two nitrogen atoms, N(1) and N(2), are below (−0.0538 and −0.0539 Å) the best least-squares plane through these four atoms. The copper atom is displaced by some 0.196 Å from the same plane towards the apical oxygen atom.

The complex molecules are linked together through hydrogen bonds. The distance $O_w-H...O(22^i)$ ($i; \frac{1}{2}-x, y, \frac{1}{2}+z$) amounts to 2.818(9) Å. The crystal structure confirms, fairly well, theoretical predictions;[9] the ring conformations in the chelated molecule can be assigned as 8–5 in our notation. These ring conformations have the lowest energy of all equatorial conformations of the *N*,*N*-dimethylisoleucine chelate ring. In addition the energies of both chelate rings are almost equal, differing by less than 0.5 kJ mol^{-1} ($\Delta V = 0.39$ kJ mol^{-1}, $\Delta G = 0.17$ kJ mol^{-1}). The next most stable equatorial conformation of the chelate ring (6 in our notation) has about a 2 kJ mol^{-1} higher conformation energy. The chelate rings do not assume one of the energetically (up to 10 kJ mol^{-1}) favourable axial conformations; this can be easily explained by the fact that the apically bound water molecule mitigates against the formation of such conformations due to close contacts with the side chain of the ligand.

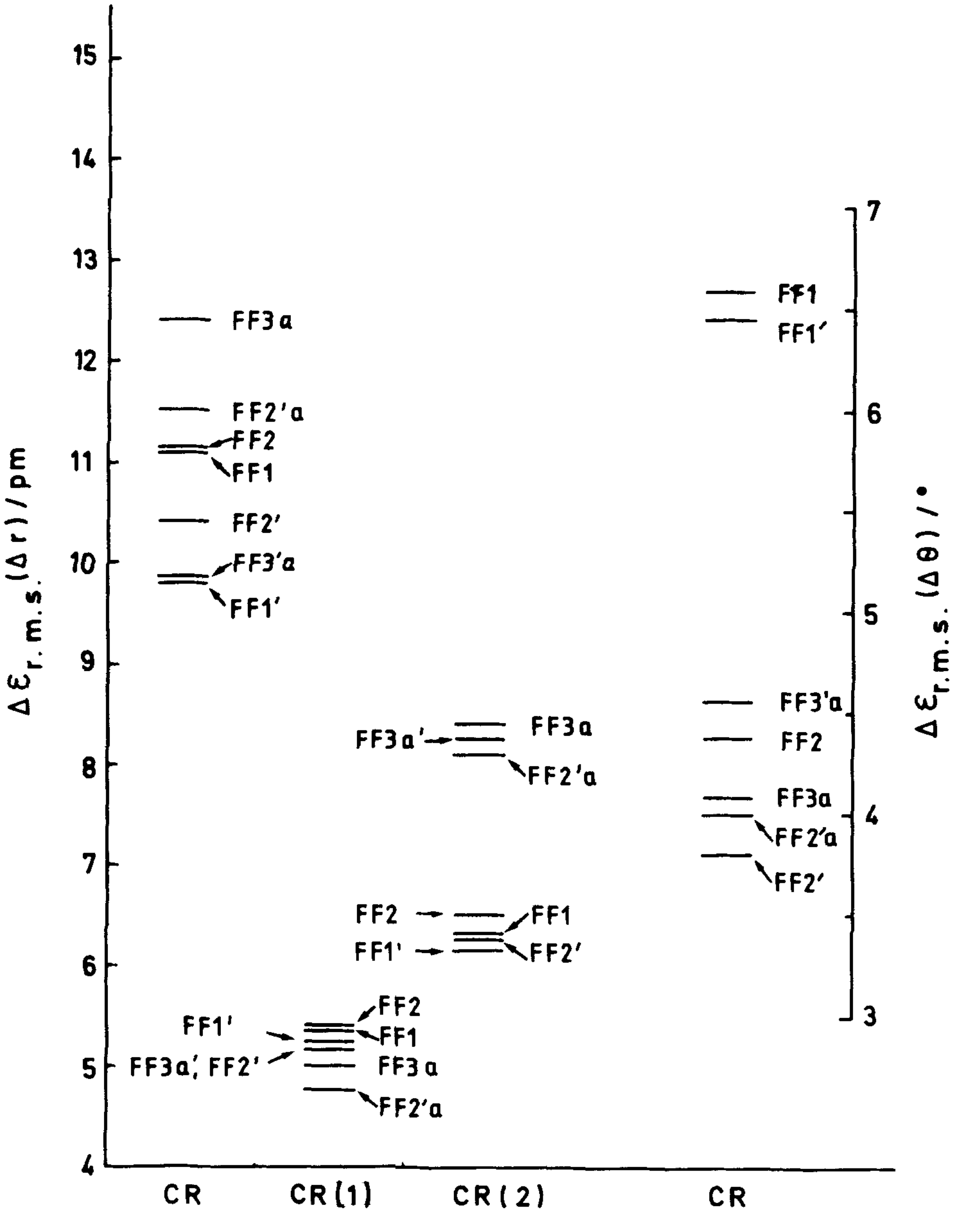

FIGURE 2 Comparison of X-ray molecular structure with theoretically predicted conformations. CR: molecular conformation in crystal, chelate rings (1) and (2) having the conformation CR; FF1, FF2 *etc.*: *conformations obtained with respective force fields (see Table I)*; $\varepsilon_{r.m.s.}$ *(Δr)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

As can be seen by comparison of crystal and theoretical structures ($\varepsilon_{r.m.s.}(\Delta r)$, Fig. 2) obtained by various force fields (Table I), the various sets of empirical parameters proved to be nearly equally as good in predicting the crystal geometry of this complex as for *bis*-(*N*,*N*-dimethylvalinato)copper(II). Force fields with additional out-of-plane bending potentials for the carboxylic oxygen did not yield a substantially better general agreement with the crystal structure; only better $\varepsilon_{\mathrm{r.m.s.}}$ values for angles were obtained (Ring(1): 24.8° for FF2', compared to 3.9° for FF2a' and 6.7° for crystal structure; Ring(2): 23.4° for FF2', compared to 3.3° for FF2a' and 2.2° for crystal structure).

TABLE I
Parameters for force-field calculations.*

Internal coordinate	Empirical parameters k_θ, k_χ/(kcal mol^{-1} rad^{-2})				
	FF1	FF2	FF2a	FF3	FF3a
N-Cu-O	97.784	97.784	97.784	11.0	11.0
X-Cu-O	97.784	9.0	9.0	11.0	11.0
X-Cu-N	97.784	9.0	9.0	11.0	11.0
χ			50.0		100.0

*FF1, force field from Ref. 1; FF2, FF3 asymmetrical and symmetrical force fields, respectively, taken from Ref. 8; X, apically coordinated "dummy" oxygen atom. For all force-fields $\theta_0 = \pi/2$. In force field denoted by an apostrophe, a non-bonding potential is applied to the apical oxygen atom (X ≡ O).

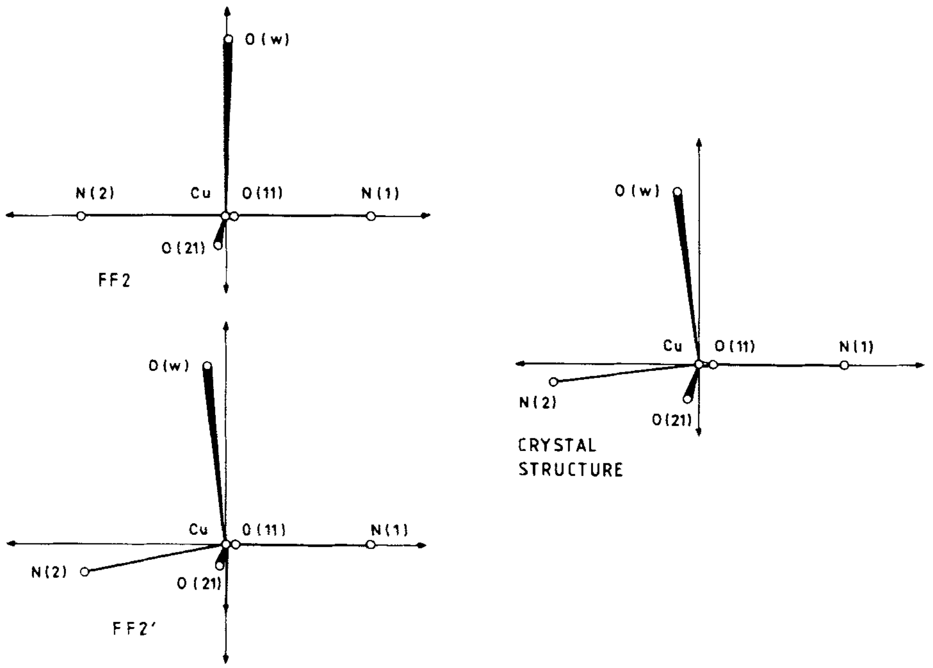

FIGURE 3 Copper coordination polyhedron obtained by two force fields (left) compared with experimental structure (right). Assignment of a nonbonding potential to atom O(w) (force field FF2') results in a better agreement between theory and experiment.

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 $U_{eq}(\times 10^4)$.[a]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}(Å^2)
Cu	12031(3)	8740(6)	−1027(17)	390(3)
O_w	1932(3)	536(4)	2829(11)	626(21)
N(1)	1613(2)	1969(4)	−1304(10)	384(16)
O(11)	695(2)	1705(3)	1365(9)	487(16)
O(12)	636(2)	3108(3)	2519(10)	553(18)
C(11)	888(3)	2509(5)	1478(13)	421(21)
C(12)	1519(3)	2660(4)	499(12)	367(19)
C(13)	1662(3)	3635(4)	−193(14)	471(21)
C(14)	1912(4)	4131(5)	1865(16)	657(28)
C(15)	2552(5)	3835(8)	2517(25)	1052(57)
C(16)	1140(4)	4155(6)	−1208(17)	679(32)
C(17)	2267(3)	1845(5)	−1824(14)	491(23)
C(18)	1286(3)	2166(6)	−3354(13)	561(27)
N(2)	711(2)	−205(4)	737(10)	401(17)
O(21)	1571(2)	59(3)	−2222(9)	479(16)
O(22)	1912(2)	−1317(4)	−2269(12)	748(23)
C(21)	1562(3)	−744(5)	−1541(14)	497(24)
C(22)	1117(3)	−986(4)	316(13)	437(20)
C(23)	810(3)	−1902(4)	141(18)	563(25)
C(24)	1204(4)	−2618(5)	1324(21)	690(32)
C(25)	893(5)	−3475(6)	1762(29)	1105(56)
C(26)	646(4)	−2168(6)	−2202(21)	850(42)
C(27)	503(3)	−193(5)	3080(13)	490(25)
C(28)	169(3)	−170(5)	−681(13)	478(23)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j\Sigma_{ij}a^*_ia^*_ja_ia_j$

Theoretical predictions for one of the chelate rings (Ring 1) are in a better agreement with experimental findings, (irrespective of the force field employed, than is the case with the other ring (Ring 2). This is probably due to intermolecular interactions in the crystal lattice; the intermolecular hydrogen bond O(w)... O(22) is expected to be the most important. Theoretical values for the torsion angle C(22)-C(23)-C(24)-C(25) deviate by a high (14°) and constant (within $< 0.5°$) amount from the experimentally observed value, irrespective of the empirical parameters used. This is additional support for the assumed role of intermolecular interactions in distorting Ring 2.

The geometry of the coordination polyhedron is better reproduced by "weak" force fields (FF2 and FF3) than by the "strong" one (FF1). These "weak" force fields yield minima with distinctly lower values of $\varepsilon_{\mathrm{r.m.s.}}(\theta)$, which is in accordance with our previous conclusions.[6–8] The assignment of a non-bonding potential to the apically coordinated oxygen (hydrogen atoms being disregarded as a first approximation) leads, in almost all cases, to a better agreement between theory and experiment (Fig. 3). This clearly shows that the shape of the copper coordination polyhedron is influenced by non-bonding interactions of the ligated water molecule with the chelate rings as well. In conclusion, it can be stated that force field used here fairly well reproduces the geometry of the title compound with respect both to ring conformation and copper coordination (Table III, Fig. 4). Although the theoretical calculations and crystallographic results strongly suggest the existence of intermolecular interactions which influence the conformation of the molecule, a detailed quantitative analysis of these interactions is not yet possible.

TABLE III
Interatomic distances (Å), angles (°) and selected torsion angles (°).

Ring(1)	Ring(2)		Difference Ring(1): Ring(2)	Theoretical value*	Difference: Exp.-theor.
Cu-O(w)		2.448(6)		2.475	−0.027
Cu-O(11)		1.900(5)		1.947	−0.047
			0.051		
	Cu-O(21)	1.949(5)		1.947	0.002
Cu-N(1)		2.014(5)		1.998	0.016
			−0.005		
	Cu-N(2)	2.019(5)		1.999	0.020
O(11)-C(11)		1.284(9)		1.286	−0.002
			0.009		
	O(21)-C(21)	1.275(9)		1.286	−0.011
O(12)-C(11)		1.233(9)		1.240	−0.007
			−0.005		
	O(22)-C(21)	1.238(9)		1.240	−0.002
N(1)-C(12)		1.519(9)		1.489	0.030
			0.017		
	N(2)-C(22)	1.502(8)		1.489	0.013
N(1)-C(17)		1.496(8)		1.484	0.012
			0.010		
	N(2)-C(27)	1.486(10)		1.484	0.002
N(1)-C(18)		1.463(9)		1.479	−0.016
			−0.012		
	N(2)-C(28)	1.475(9)		1.479	−0.004
C(11)-C(12)		1.534(9)		1.534	0.000
			−0.003		
	C(21)-C(22)	1.537(10)		1.534	−0.003
C(12)-C(13)		1.556(9)		1.569	−0.013
			0.017		
	C(22)-C(23)	1.539(9)		1.567	−0.028
C(13)-C(14)		1.550(12)		1.554	−0.004
			−0.009		
	C(23)-C(24)	1.559(12)		1.554	0.005
C(14)-C(15)		1.537(14)		1.549	−0.012
			0.052		
	C(24)-C(25)	1.485(13)		1.547	−0.062
C(13)-C(16)		1.523(11)		1.554	−0.031
			0.010		
	C(23)-C(26)	1.513(16)		1.555	−0.042
O(11)-Cu-N(1)		84.1(2)		86.7	−2.6
			0.7		
	O(21)-Cu-N(2)	83.4(2)		86.7	−3.3
Cu-O(11)-C(11)		116.5(4)		112.8	4.7
			4.3		
	Cu-O(21)-C(21)	112.2(5)		112.7	−0.5
Cu-N(1)-C(12)		113.9(4)		103.3	10.6
			8.7		
	Cu-N(2)-C(22)	105.2(4)		103.2	2.0
Cu-N(1)-C(17)		114.3(4)		111.0	3.3
			0.9		
	Cu-N(2)-C(27)	113.4(4)		110.9	2.5
Cu-N(1)-C(18)		104.3(4)		104.8	−0.5
			−1.1		
	Cu-N(2)-C(28)	105.4(4)		104.9	0.5
N(1)-Cu-O(w)		97.6(4)		95.7	2.9
			7.1		

N(2)-Cu-O(w)	90.5(2)		95.8	−5.3
O(11)-Cu-O(w)	101.0(2)	7.1	94.3	6.7
O(21)-Cu-O(w)	93.9(2)		94.4	−0.5
O(11)-Cu-O(21)	165.1(2)	6.8	171.3	−6.2
N(1)-Cu-N(2)	171.9(2)		168.5	3.4
N(1)-Cu-O(21)	95.1(2)		92.4	2.7
N(2)-Cu-O(11)	95.2(2)		92.5	2.7
C(12)-N(1)-C(17)	111.6(5)	0.8	111.7	−0.1
C(22)-N(2)-C(27)	110.8(5)		111.8	−1.8
C(12)-N(1)-C(18)	113.5(5)	−1.2	114.4	−0.9
C(22)-N(2)-C(28)	114.7(5)		114.5	0.2
O(11)-C(11)-O(12)	124.3(6)	2.0	119.5	4.8
O(21)-C(21)-O(22)	122.3(7)		119.6	2.7
O(11)-C(11)-C(12)	115.0(6)	−3.0	115.6	−0.6
O(21)-C(21)-C(22)	118.0(6)		115.5	2.5
O(12)-C(11)-C(12)	120.1(6)	0.4	124.8	−4.7
O(22)-C(21)-C(22)	119.7(6)		124.8	−5.1
N(1)-C(12)-C(11)	107.4(5)	−1.4	109.9	−2.5
N(2)-C(22)-C(21)	108.8(5)		109.9	−1.1
N(1)-C(12)-C(13)	115.2(6)	−1.3	114.3	0.9
N(2)-C(22)-C(23)	116.5(5)		114.5	2.0
C(11)-C(12)-C(13)	115.3(5)	−1.2	114.3	1.0
C(21)-C(22)-C(23)	116.5(6)		114.3	2.2
C(12)-C(13)-C(14)	108.1(6)	−1.7	111.1	−3.0
C(22)-C(23)-C(24)	109.8(6)		109.4	0.4
C(12)-C(13)-C(16)	115.9(6)	1.9	114.5	1.4
C(22)-C(23)-C(26)	114.0(8)		114.0	0.0
C(14)-C(13)-C(16)	110.3(6)	−2.0	109.2	1.1
C(24)-C(23)-C(26)	112.3(7)		110.3	2.0
C(13)-C(14)-C(15)	113.3(8)	−1.6	111.8	1.5
C(23)-C(24)-C(25)	114.9(8)		111.9	3.0
C(17)-N(1)-C(18)	109.1(6)	1.5	111.1	−2.0
C(27)-N(2)-C(28)	107.4(5)		111.0	−3.6
O(11)-Cu-N(1)-C(17)	151.4(5)	−0.7	144.3	7.1
O(21)-Cu-N(2)-C(27)	152.1(5)		144.1	8.0
C(13)-C(12)-N(1)-Cu	−166.7(4)	−4.2	−165.2	−1.5
C(23)-C(22)-N(2)-Cu	−162.4(6)		−165.6	3.2
C(16)-C(13)-C(12)-N(1)	88.7(8)	−4.1	88.5	−0.2
C(26)-C(23)-C(22))N(2)	92.8(8)		88.0	4.8
O(11)-C(11)-C(12)-N(1)	28.0(8)	20.3	33.2	−5.2
O(21)-C(21)-C(22)-N(2)	7.7(8)		33.9	−26.2
C(15)-C(14)-C(13)-C(12)	71.5(9)		73.7	−2.2

		94.0		
C(25)-C(24)-C(23)-C(22)	165.5(10)		177.1	−11.6
Cu-O(11)-C(11)-C(12)	−2.8(8)		−11.6	6.8
		−21.6		
Cu-O(21)-C(21)-C(22)	18.8(8)		−12.4	31.2
C(11)-O(11)-Cu-N(1)	−16.4(5)		−8.0	8.4
		12.4		
C(21)-O(21)-Cu-N(2)	−28.8(5)		−7.5	−21.3

* Theoretical structure conformation obtained by minimization with FF2′a. (Table I).

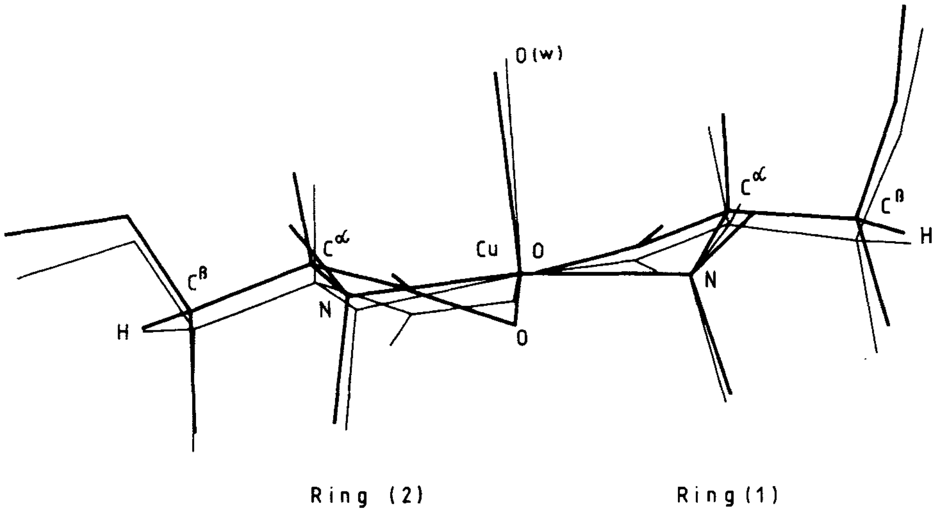

FIGURE 4 Comparison of experimental X-ray and theoretically computed (force field FF2′a) structures; heavy line: X-ray structure; light line: theoretical structure.

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