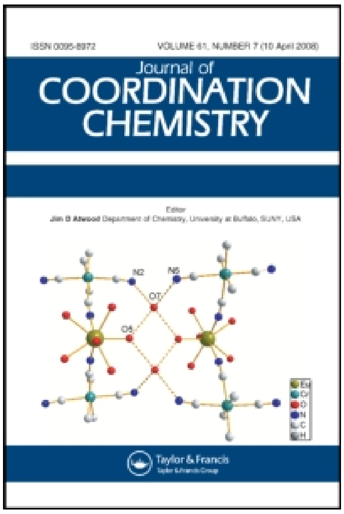

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Stereochemistry of Complexes with *N*-Alkylated Amino Acids. III. Crystal Structure and Conformational Analysis of bis-(*L-N,N*-Dimethylisoleucinato)Copper(II)

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

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The structure of the red, monoclinic modification of bis-(*L*–*N*,*N*-dimethylisoleucinato)copper(II) was solved by X-ray diffraction methods and refined to $R = 0.037$. The structure is built up of discrete molecules. The copper atom has a tetrahedrally distorted square-planar coordination involving two nitrogen atoms and two oxygen atoms in a *trans* position. The Cu–O (1.911 and 1.886 Å) and Cu–N distances (2.009 and 2.007 Å) are comparable with those in other copper(II) complexes with α-amino-acids. The conformation of the molecule corresponds to the one of the three most stable conformers, predicted theoretically. Altogether, eight theoretical molecular mechanics models were checked in order to reproduce the experimentally observed geometry, especially with respect to the shape of the coordination polyhedron. Results are in good agreement with previously published data, showing the expected fitness of the different theoretical models.

Keywords: *N*,*N*-dimethylisoleucine, copper, X-ray structure, conformational analysis, molecular mechanics

INTRODUCTION

Copper(II) chelates with *N*-alkylated and *N*,*N*-dialkylated α-amino acids can generally form three crystal modifications.[1] In the most common blue modification, copper(II) is pentacoordinate (square pyramid) or hexacoordinate (octahedron), having at the apical position(s) ligand water or carboxylic oxygen atoms of neighbouring molecules. The green modification has a cage (dimeric, "acetato-like") structure with two copper atoms bound to the same carboxylic group. The third (red) crystal modification consists of discrete *trans*-planar molecules without any noticeable apical coordination.

The title compound, bis-(*L*–*N*,*N*-dimethylisoleucinato)copper(II), forms all three crystal modifications. The blue modification was obtained by recrystallization from dichlormethane or wet benzene;[2] crystals of the green copper chelate appeared after

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slow evaporation of a xylene solution (unpublished observation); the red modification was prepared from benzene solution under extremely dry conditions (see Experimental).

The principal goal of our research is to study intramolecular interactions in these kinds of complexes. Therefore we found the red modification to be most interesting, because the interactions between molecules in the crystal lattice were presumably very weak and unspecific. Lack of additional interactions due to chelation and/or hydrogen bondings makes this kind of complexes nearly ideally suited for the study of molecular conformation in the absence of influence of solute or neighbouring molecules in the crystal lattice.

The aim of the work in this paper was to compare data obtained by X-ray analysis with the molecular mechanics (or consistent force field) method. More specifically, we have posed three questions. First, does the geometry of chelate rings correspond to the geometry of the conformer having the lowest strain energy? Secondly, is the coordination polyhedron distorted from its "ideal" (strictly planar) configuration, as expected from theoretical considerations[3,4] and an X-ray analysis of a similar complex, bis-(*L*-*N*,*N*-dimethylvalinato)copper(II)?[5] Finally, how well do the different molecular mechanics models[6–9] reproduce the crystal structure of bis-(*L*-*N*,*N*-dimethylisoleucinato)copper(II), especially the shape of its coordination polyhedron. The last question is vital in developing molecular mechanics functions for conformational analysis of coordination compounds with plastic co-ordination[10] (*i.e.*, with a much distorted coordination polyhedron). This indeed is the ultimate goal of our research efforts.

EXPERIMENTAL

The ligand, *L*–*N*,*N*-dimethylisoleucine was prepared in the usual way, *i.e.*, by methylation of *L*-isoleucine through condensation with formaldehyde and subsequent hydrogenation.[11] The blue (aquo) crystal modification of the complex was prepared by reaction of copper(II) acetate monohydrate with the ligand in CH_2Cl_2 solution. The crystals of the blue modifications were heated at 105–110°C for 2 h to obtain the red modification. The resulting crystalline substance was dissolved in dry benzene (dried over sodium); the solution, after slow evaporation over calcium chloride, yielded dark red crystals suitable for X-ray analysis.

Crystal structure analysis

Crystal data

$C_{16}H_{32}CuN_2O_4$. $M_r = 379.99$, monoclinic, space group $P2_1$, $a = 11.882(2)$, $b = 6.830(1)$, $c = 12.867(2)$ Å$\beta = 113.62(1)°$, $V = 956.7(3)$ Å^3, $D_x = 1.319$ gcm^{-3}, $Z = 2$, $F(000) = 406$, Λ(MoKα) = 0.7107 Å, $\mu = 11.61$ cm^{-1}.

Accurate cell dimensions and the crystal orientation matrix were determined on a Philips PW1100 diffractometer by a least-squares treatment of the setting angles of 22 reflections in the range of $7 < \Theta < 18°$. Crystal dimensions 0.20 × 0.29 × 0.42 mm; intensities of reflections with indices h −13 to 13, k 0 to 8, l 0 to 16, with $2 < \Theta < 27°$ measured; Θ–2Θ scans; graphite monochromized MoKα radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. A total of 2064 reflections were measured, with 1978 unique, 1856 with $I > 5\sigma(I)$ taken as observed and used in the structure solution and refinement; $R(\text{int}) = 0.022$; data corrected for Lorentz and polarization effects but not for the absorption; space group $P2_1$ from systematic absences ($0k0$, $k = 2n + 1$) and structure determination. The coordinates of the Cu atom were determined from a detailed analysis of the Patterson map and the coordinates of the remaining non-hydrogen atoms found *via* Fourier syntheses. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, the difference map showed maxima in positions consistent with the expected locations of the hydrogen atoms; in the final rounds of calculations the hydrogen atoms were positioned on geometrical grounds (C–H 1.08 Å) and included (as riding atoms) in the structure factor calculations with an overall U(iso). The final cycle of refinement included 208 variable parameters; $R = 0.037$; $R_w = 0.042$, $S = 1.798$, $w = 1.743/(\sigma^2(F_o) + 0.000615(F_o)^2)$; Max. shift/error = 0.056; maximum and minimum densities in the final difference map +0.47 and −0.37 eÅ^{-3}, respectively; no chemically significant features. Scattering factors and anomalous dispersion corrections were from International Tables for X-ray Crystallography.[12] All calculations were performed on an IBM PC/AT compatible microcomputer (microprocessor 80386/25 MHz and mathematical coprocessor 80387) using the CRYSRULER PACKAGE.[13] Atomic coordinates are given in Table I and a view of the molecule prepared using the ORTEP II programme[14] in Fig. 1. Lists of hydrogen positions, anisotropic temperature factors and observed and calculated structure factors are available from N.R. upon request.

TABLE I

Final atomic coordinates for non-hydrogen atoms ($\times 10^4$, $\times 10^5$ for Cu) and equivalent isotropic thermal parameters U_{eq} ($\times 10^3$, $\times 10^4$ Å^2 for Cu) with e.s.d.'s in parentheses for $C_{16}H_{32}CuN_2O_4$.*

Atom	x/a	y/b	z/c	U_{eq}
Cu	17888(4)	0	25373(4)	438(2)
O11	1623(4)	−2063(5)	1482(3)	50(1)
O12	1953(4)	−2812(7)	−49(3)	63(1)
O21	2000(6)	2007(7)	3606(4)	86(3)
O22	1690(10)	2772(9)	5153(6)	145(6)
N1	2313(3)	1605(6)	1500(3)	41(1)
N2	861(4)	−1334(8)	3340(4)	58(2)
C11	2064(4)	−1724(8)	741(4)	45(2)
C12	2805(4)	197(10)	895(3)	41(1)
C13	4196(4)	−212(10)	1497(4)	47(2)
C14	4627(5)	−1439(11)	742(6)	68(2)
C15	6055(6)	−1343(13)	1138(7)	84(3)
C16	4572(5)	−1100(11)	2668(5)	63(2)
C17	1111(5)	2374(9)	666(6)	62(2)
C18	3129(5)	3311(8)	1999(5)	55(2)
C21	1703(10)	1582(11)	4470(7)	89(4)
C22	1388(8)	−539(10)	4530(6)	69(3)
C23	2504(9)	−1712(14)	5348(6)	95(4)
C24	2988(13)	−982(22)	6589(8)	152(7)
C25	2301(11)	−1304(22)	7158(9)	143(7)
C26	3578(8)	−1687(20)	4982(7)	130(6)
C27	−391(6)	−595(19)	2734(7)	108(5)
C28	810(10)	−3515(11)	3278(7)	94(4)

*Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $U_{eq} = 1/3\ \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

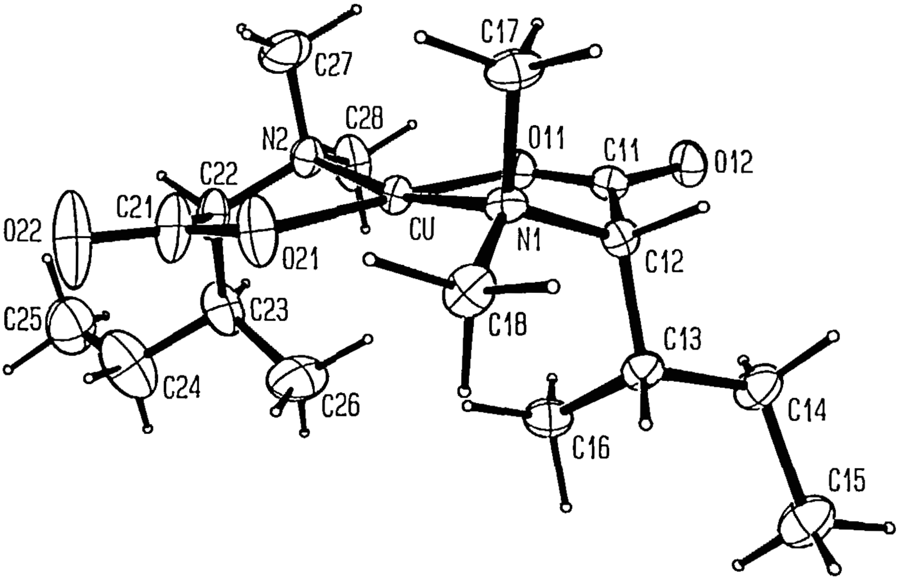

FIGURE 1 An ORTEP plot of bis-(*L*-*N*,*N*-dimethylisoleucinato)copper(II). Thermal ellipsoids correspond to 20% probability.

Conformational analysis

The conformational (strain) potential energy was calculated from the basic formula:

$$V = 1/2\sum_{i} k_{b,i}(b_i - b_{o,i})^2 + 1/2\sum_{j} k_{\theta,j}(\theta_j - \theta_{o,j})^2 + 1/2\sum_{k} V_n(1 \pm \cos n\,\varphi_k)$$

$$+ \sum_{l}(A_l \exp(-B_l\, r_l) - C_l r_l^{-6}) + 1/2\sum_{m} k_{\chi,m}\,\chi_m^{2} + 1/2\,k_\beta(\beta - \beta_o)^2 + V_{XMY} + V_{el} \qquad (1)$$

in which b, θ, φ, and χ stand for bond lengths, valence, torsional and out-of-plane angles, respectively; r is the non-bonded distance, and β is a distortion coordinate defined as an angle between bisectors of two opposite (N-Cu-O and N′-Cu-O′) valence angles about copper. K_b is an empirical parameter for bond stretching and k_0 for valence angle bending. Torsional interactions were determined with parameters V_n and n (height and multiplicity of the 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 the carboxyl groups with a quadratic function dependent on the parameter k_χ was also computed.

For distortion of the coordination polyhedron we proposed altogether three kinds of models (Table II), a "dummy" atom model (FF1–FF3a),[6] a model with distortion coordinate potential (M3–M5),[7,8] and an electrostatic model (M6).[9] These models were determined by the last three terms of equation (*1*). The quadratic potential dependent on the distortion coordinate β and parameters k_β and β_o is specific for force fields M3–M5.[7,8] The potential V_{XMY} is the angle-bending potential for the angles around copper, which can be quadratic (FF1, FF2, FF3, FF3a, M3) or in the form of a cosine power series (M4, M5); see below (equations (*2*) and (*3*)). V_{el} is the coulombic potential between four ligand (denoted as Y) atoms and two point charges (denoted as X), which are situated above and below the plane of the chelate rings (model M6).[9] The potential dependent on the atoms around copper, when using the "dummy" atom model (FF1, FF2, FF3 and FF3a), is determined only by quadratic angle-bending interactions between four "real" and two "dummy" apically placed atoms.

TABLE II
Parameters for force-field calculations.*

	Bonding potential	
Bond	k_b(kcal $mol^{-1}Å^{-2}$)	b_o(Å)
Cu–N (all models)	251.65	2.000
Cu–O (all models)	270.00	1.950
Cu–X (FF1–FF3a)	270.00	2.475
‡ (M6)	14.0101	0.0
	Angle-bending and out-of-plane deformation potential	
Angle	k_θ,k_χ (kcal mol^{-1} rad^{-2}) ‡	θ_o(rad)
N–Cu–O (M3)	250.00	1.571
(FF1, FF2)	97.784	1.571
(FF3, FF3a)	11.00	1.571
X–Cu–Y (FF1)	97.784	1.571
(FF2)	9.0	1.571
(FF3, FF3a)	11.0	1.571
χ (FF3a, M3–M6)	100.0	
	k_z(kcal mol^{-1})	k_s(kcal mol^{-1})
N–Cu–O (M4)	500.00	
(M5)	180.00	
Y–Cu–Y (M5)		22.50
	Distortion potential	
	k_β (kcal mol^{-1} rad^{-2}) ‡	β_o (rad)
β (M3–M5)	37.50	3.142
	Coulombic potential	
Point charges	q (e)	
X (M6)	−0.750	
Y (M6)	−0.375	

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* "Dummy" atom is denoted by X, and ligand atoms (O, N) by Y. Only the most specific parameters are presented here, other parameters are from ref. 6; 1 cal = 4.184 J.

The two-well angle-bending potential for the N–Cu–O angle (with minima at 90° and 109.47°) is given by expression (*2*),

$$V_z = 1/2\, k_z\, (9z^4 + 6z^3 + z^2) \qquad (2)$$

where k_z is an empirical parameter (Table II) and $z = \cos\theta$. For the angles N–Cu–N and O–Cu–O (with minima at 109.47° and 180°) the two-well angle-bending function has the form

$$V_s = 1/2\, k_s(9/8\, s^4 + 3\sqrt{2}/2\, s^3 + s^2) \qquad (3)$$

where k_s is an empirical parameter (Table II) and $s = \sin\theta$. Both potentials, V_z and V_s, have two minima of equal (zero) energy with a symmetrical maximum between them. The parameters for the potential (*3*) were chosen so that potential (*3*) had the same maximum value as potential (*2*).

Calculations were performed with a programme developed by Rasmussen and coworkers,[15] further modified to cope with new empirical potentials.

Root-mean-square deviations between crystal and theoretical structures were calculated from

$$\varepsilon_{r.m.s.}(\Delta X) = (1/N \sum_{i=1}^{n} (\Delta X_i)^2)^{1/2} \qquad (4)$$

where X stands for angles around copper (valence angles, θ, distortion angle, β, and "torsional angle", φ(ONNO)), when comparing the copper coordination geometry, or the interatomic distance, r, when checking the overall similarity. Δ denotes the difference between the values of the observable, X, in two structures.

RESULTS AND DISCUSSION

The structure of bis-(*L*-*N*,*N*-dimethylisoleucinato)copper(II) (Fig. 1 and Tables I and III) is built up of discrete molecules. The copper atom has distorted square planar coordination involving two oxygen and two nitrogen atoms in a *trans* position. It is also apparent that there is no significant interaction between copper and any other atom. The Cu–N and Cu–O bond distances (Table III) are comparable with previously reported data for some α-amino acidate copper complexes.[2,5] *Trans* (N–Cu–N and O–Cu–O) angles are close to the corresponding angles found in *N*,*N*-dimethylvalinato[5] and *N*-(4-toluene-sulphonyl)leucinato complexes.[16] The displacement of the copper atom from the basal least-squares plane calculated through O11,O21,N1 and N2 is 0.1352(3) Å. The oxygen atoms are below (−0.102(3) and −0.228(4) Å) while the nitrogens are above (0.077(2) and 0.137(3) Å) the plane. There are no significant interactions between neighbouring molecules. The closest contact is 3.32(1) Å, between 0.21... C28^i($i = x, y + 1, z$).

The conformations of the two chelate rings are not the same. According to our notation[4] Ring 1 has conformation 12 and Ring 2 conformation 15; therefore, overall molecular conformation should be denoted as 12–15. Conformation 12–15 belongs to the set of three conformations with the lowest strain energy (15–15: 27.06; 12–15: 27.28; 12–12: 27.50 kJ mol^{-1}; calculated with FF1)[4] and therefore can be regarded as a global minimum of conformational potential. Conformations of both chelate rings were reproduced equally well using the different force fields (Fig. 2).

TABLE III
Selected bond distances (Å) and angles (°) for the complex.

Internal coordinate	Crystal structure	Theoretical structure FF3a	M5	M6
Cu-O11	1.911(4)	1.960	1.944	2.005
Cu-O21	1.886(5)	1.962	1.946	2.007
Cu-N1	2.009(4)	1.999	1.988	2.044
Cu-N2	2.007(4)	1.998	1.987	2.043
O11-C11	1.280(8)	1.289	1.296	1.290
O12-C11	1.223(7)	1.241	1.241	1.241
O21-C21	1.326(13)	1.289	1.296	1.291
O22-C21	1.202(12)	1.241	1.241	1.241
N1-C12	1.496(7)	1.487	1.490	1.487
N1-C17	1.496(6)	1.482	1.482	1.482
N1-C18	1.487(6)	1.484	1.484	1.483
N2-C22	1.504(9)	1.486	1.490	1.486
N2-C27	1.465(9)	1.483	1.482	1.483
N2-C28	1.492(9)	1.484	1.484	1.483
C11-C12	1.548(8)	1.525	1.539	1.526
C12-C13	1.544(6)	1.563	1.563	1.563
C13-C14	1.519(10)	1.555	1.555	1.555
C13-C16	1.516(8)	1.551	1.550	1.551
C14-C15	1.565(9)	1.547	1.547	1.547
C21-C22	1.506(11)	1.524	1.538	1.525
C22-C23	1.546(11)	1.564	1.564	1.564
C23-C24	1.547(13)	1.555	1.555	1.555
C23-C26	1.527(16)	1.550	1.550	1.550
C24-C25	1.315(21)	1.547	1.547	1.547
N1-Cu-N2	166.0(2)	159.9	161.0	160.2
O21-Cu-N2	83.9(2)	83.7	87.6	82.1
O21-Cu-N1	95.8(2)	95.9	93.6	98.9
O11-Cu-N2	96.3(2)	95.7	93.4	98.5
O11-Cu-N1	84.4(2)	83.8	87.7	82.2
O11-Cu-O21	178.3(2)	177.4	173.3	175.5
Cu-O11-C11	116.1(3)	114.2	110.9	114.6
Cu-O21-C21	116.7(5)	114.2	110.8	114.5
Cu-N1-C18	117.6(3)	113.1	115.1	112.3
Cu-N1-C17	102.0(3)	103.6	103.3	103.6
Cu-N1-C12	106.5(3)	106.9	104.5	107.3
C17-N1-C18	107.7(4)	109.0	109.1	109.0
C12-N1-C18	113.9(4)	113.8	114.2	114.0
C12-N1-C17	108.2(4)	110.1	110.0	110.1
Cu-N2-C28	116.4(5)	113.7	115.6	112.9
Cu-N2-C27	102.7(5)	103.4	103.1	103.5
Cu-N2-C22	105.7(4)	106.7	104.3	107.1
C27-N2-C28	107.7(7)	108.8	108.9	108.9
C22-N2-C28	114.0(5)	113.7	114.2	113.9
C22-N2-C27	109.7(6)	110.1	110.1	110.2
O11-C11-O12	124.7(5)	121.3	120.5	121.1
O12-C11-C12	119.2(5)	123.0	122.2	122.8
O11-C11-C12	116.1(4)	115.7	117.2	116.1
N1-C12-C11	106.9(4)	106.8	108.2	107.0
C11-C12-C13	110.5(5)	109.4	109.1	109.4

TABLE III (continued)

Internal coordinate	Crystal structure	Theoretical structure FF3a	M5	M6
N1-C12-C13	114.7(4)	114.8	114.7	114.8
C12-C13-C16	113.6(4)	112.0	111.9	112.0
C12-C13-C14	110.3(4)	109.5	109.6	109.6
C14-C13-C16	112.0(5)	110.3	110.3	110.3
C13-C14-C15	111.6(6)	111.9	111.9	111.9
O21-C21-O22	123.4(8)	121.4	120.6	121.2
O22-C21-C22	122.5(8)	123.1	122.3	122.9
O21-C21-C22	114.1(7)	115.5	117.1	115.9
N2-C22-C21	107.8(6)	106.8	108.1	107.0
C21-C22-C23	111.7(7)	109.3	109.1	109.4
N2-C22-C23	113.6(6)	114.6	114.5	114.6
C22-C23-C26	112.3(7)	112.4	112.3	112.4
C22-C23-C24	113.5(9)	111.9	112.0	111.9
C24-C23-C26	107.7(8)	108.4	108.4	108.4
C23-C24-C25	117.6(10)	112.3	112.3	112.3
O21-Cu-N2-C27	88.3(5)	91.0	92.4	90.9
O11-Cu-N1-C17	88.4(3)	91.9	93.2	91.8
N1-Cu-O11-C11	10.6(4)	5.7	3.5	5.9
N2-Cu-O21-C21	11.9(6)	6.3	4.0	6.5
Cu-O11-C11-C12	7.2(6)	15.1	16.8	15.0
Cu-O21-C21-C22	7.2(10)	14.9	16.7	14.8
Cu-N1-C12-C13	−90.2(4)	−85.2	−88.3	−84.8
Cu-N2-C22-C23	−88.7(7)	−84.1	−87.2	−83.6
O11-C11-C12-N1	−27.6(6)	−35.0	−35.7	−35.4
N1-C12-C13-C16	60.7(6)	62.1	63.2	62.1
C12-C13-C14-C15	162.3(5)	170.8	170.9	170.9
O21-C21-C22-N2	−29.4(10)	−35.5	−36.2	−35.9
N2-C22-C23-C26	61.7(10)	60.0	61.4	60.2
C22-C23-C24-C25	70.3(14)	60.7	60.9	60.9
β	171.8	164.8	171.5	169.8
O11-N1-N2-O21	163.5(3)	162.2	154.3	155.5

This provides additional support for the observation that there were no noticeable intramoleuclar interactions in the crystal lattice. The $\varepsilon_{\mathrm{r.m.s.}}$ (Δr) values range from 0.06 to 0.08 Å and correspond roughly to root-mean-square deviations in other similar molecules.[2,5]

The proof of the validity of our empirical force-field models is to see how well they reproduce the shape of the coordination polyhedron. R.m.s. deviations with respect to angles around copper (Fig. 2) are the lowest for force fields FF3, FF3a and M6. The force fields based on distortion angle potential (M3, M4 and M5) yielded a less successful reproduction of N–Cu–O angles than the other force fields (Table III). Qualitative comparison of theoretical structures (Fig. 3) shows that all force fields based on the "dummy" atom model (FF1, FF2, FF3 and FF3a) yielded a distorted pyramid. On the contrary, the force fields based on the distortion coordinate potential (M3, M4 and M5) and on the electrostatic model (M6) gave the same kind of coordination polyhedron as observed in crystal structure (*i.e.*, a flattened tetrahedron).

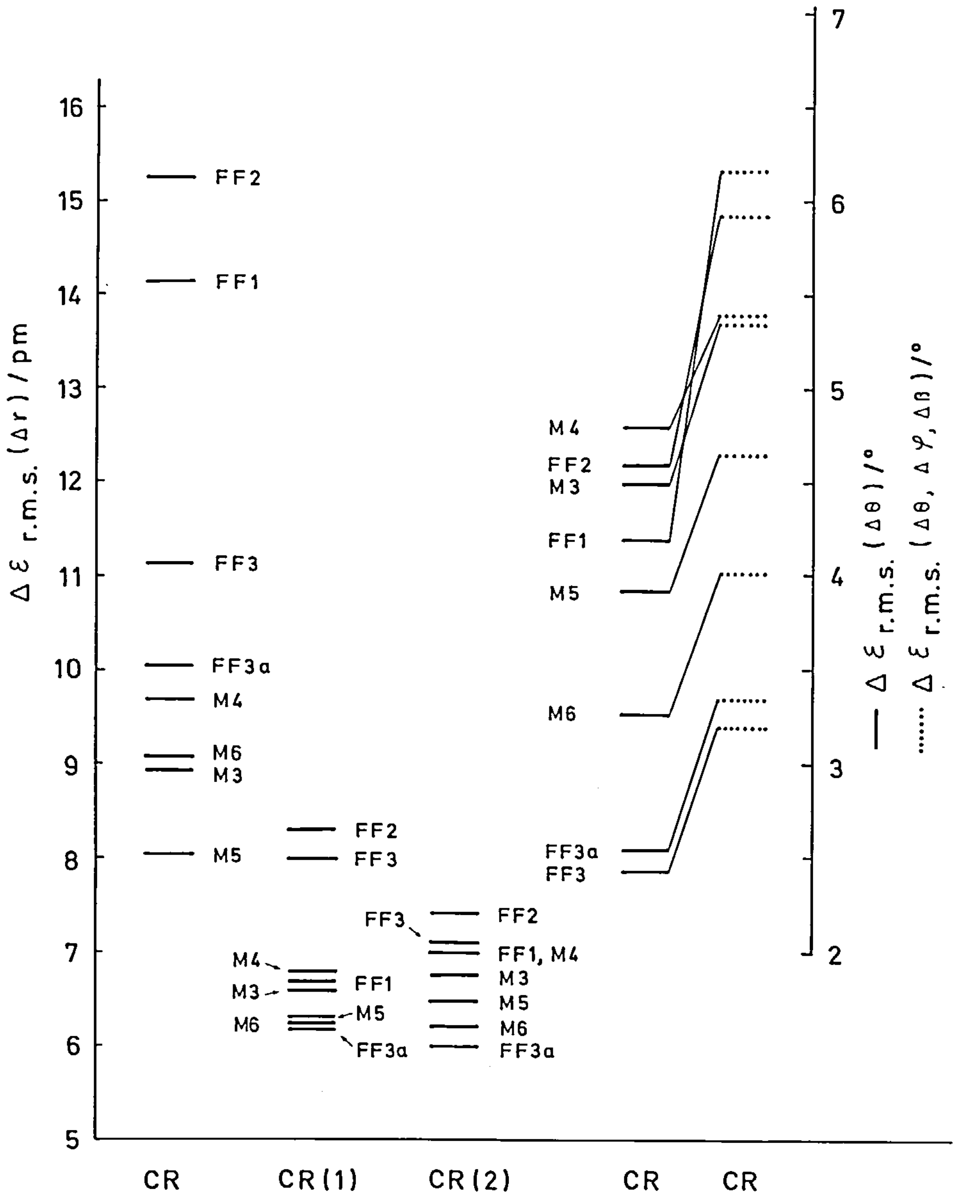

FIGURE 2 Comparison of X-ray molecular structure with theoretically predicted geometry. CR: molecular conformation in crystal, chelate rings (1) and (2) having the conformation CR(1) and CR(2); FF1, FF2, *etc.*: conformations obtained with respective force fields (see Table II); $\varepsilon_{r.m.s.}$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

It can be concluded that the application of molecular mechanics models to interpret the crystal structure of bis-(*L*-*N*,*N*-dimethylisoleucinato)copper(II) confirms our earlier findings$^{7-9}$ that the force fields based on the "dummy" atom

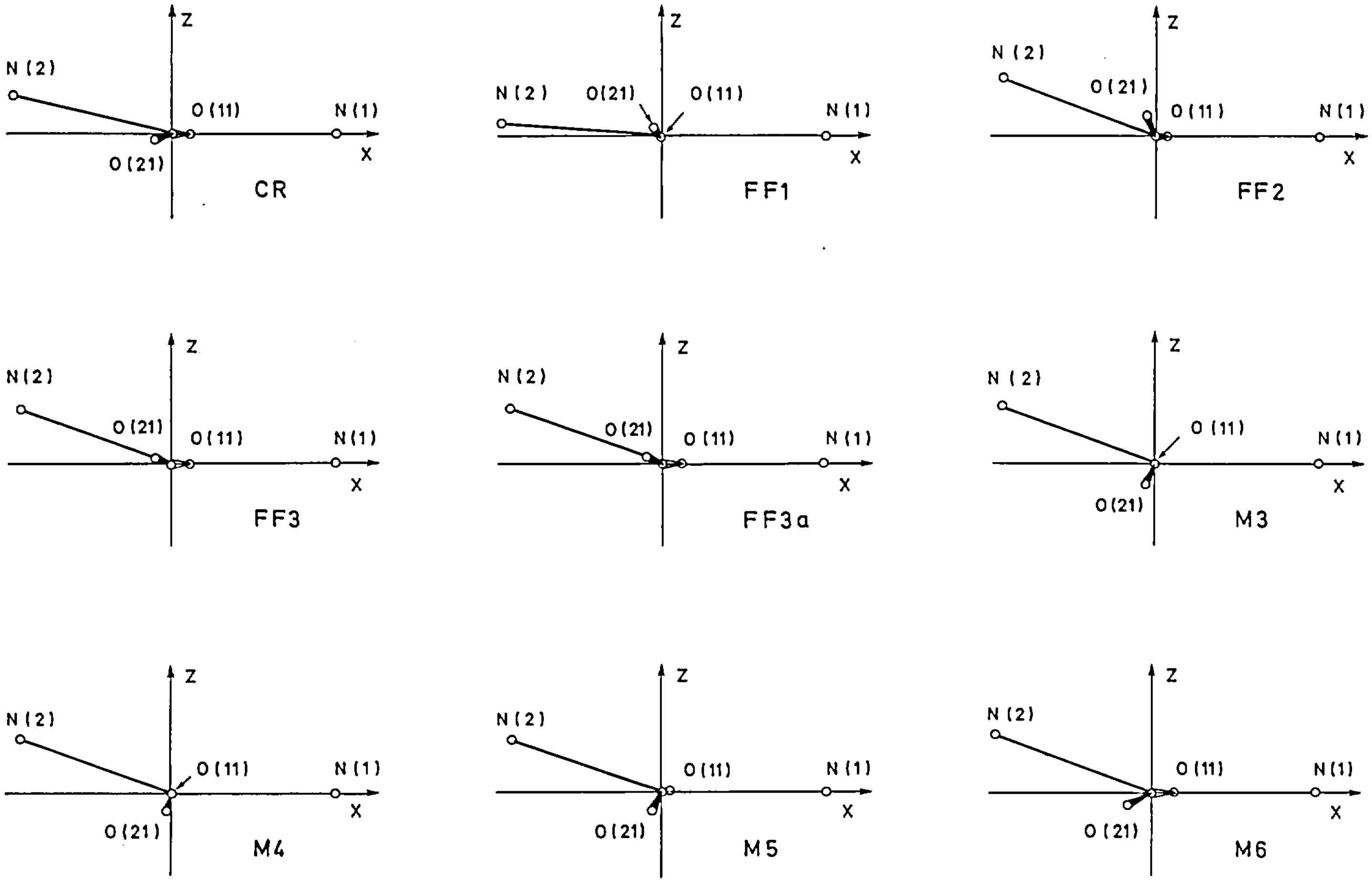

FIGURE 3 Copper coordination polyhedron in the crystal structure (CR), and as obtained with the various empirical force fields (FF1, FF2 *etc.*). For explanation, see Table II and Experimental.

model are not suitable for calculations on copper complexes with distorted geometry. The force fields based on the other two models appeared to be capable of reproducing the right shape for the coordination polyhedron, but yield, to some degree, a less successful reproduction of angles around the copper atom. In spite of this fact, which can be easily attributed to imperfections in the parametrization procedure, we recommend models based on distortion coordinate potential and electrostatic interactions for further improvement.

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