CROATICA CHEMICA ACTA CCACAA **69** (3) 1189–1200 (1996)

ISSN-0011-1643
CCA–2368
Original Scientific Paper

An Analysis of the Shape of the Coordination Polyhedron of Pentacoordinated Copper(II) Chelates with *N*-Alkylated Amino Acids

Nenad Raos

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

Received October 24, 1995; revised December 11, 1995; accepted December 11, 1995

An analysis of eight pentacoordinated (aqua) copper(II) chelates with *N*-alkylated amino acids revealed that they could be separated in two groups with respect to the shape of their coordination polyhedra. Group I, consisting of *N,N*-dimethylated derivatives, can be described as distorted square pyramids with a pseudo C_{4v} symmetry. Group II, consisting of other *N*-alkylated and *N,N*-dialkylated derivatives, can be described as square pyramids distorted towards the trigonal pyramid along the axis O-Cu-O' = 180°. The apical bond length (Cu-OH_2) correlates extremely well on the N-Cu-N' angle (r = 0.9996) for the group I molecules and substantially less well for group II (r = 0.954). Multiple regression of experimental apical lengths on the N-Cu-N' angle and the absolute difference |N-Cu-N' – O-Cu-O'| yields $|R|$ = 0.981 for N = 8. By applying the different measures of distortion of the copper(II) coordination polyhedron, it was possible to predict the apical bond length from the structures obtained by molecular mechanics calculations with the minimum value for the root-mean-square deviation between experiment and theory 0.083 Å (group I), 0.032 Å (group II) and 0.068 Å (both groups).

INTRODUCTION

Copper(II) chelates with *N*-alkylated amino acids[1] are a subclass of the coordination compounds of *N*-protected amino acids,[2] which were first investigated because of the enantioselectivity effect[3–5] having in mind a possible application of that effect to the ligand exchange chromatography.[6] However, the observation that the enantioselectivity effect in that class of compounds was dependent on the distortion of the copper coordination polyhedron[4,7] led to development of a number of molecular mechanics models, aimed at reproducing both the observed enantioselectivity and the proper shape of the copper(II) coordination polyhedron.[8–11] The molecular mechanics models were developed to cope with tetracoordinated copper(II) chelates, *i.e.* the ones that existed in solutions with a solute incapable of coordinating (*e.g.* chloroform). The fact that, in the physiologically most interesting solute (water), mostly pentacoordinated (aqua) complexes are present, and the fact that this class of chelates was studied crystallographically in greater depth than the tetracoordinated ones, inspired us to a attempt to throw more light on their stereochemical behaviour. During our systematic research on pentacoordinated (aqua) complexes of copper(II) with *N*-alkylated amino acids, a high variation of the apical bond ($Cu-OH_2$) length was observed,[12] which was later attributed to distortion of the coordination polyhedron.[13]

Based on the fact that apical bond length is negatively correlated with the distortion of copper(II) coordination from the chelate plane, a method was developed for estimating the $Cu-OH_2$ length from the calculated (by molecular mechanics method) distortion of the coordination polyhedron.[13] In that paper, no systematic analysis of distortion of the copper(II) coordination polyhedron was given; the aim of this paper is to make such an analysis in order to improve the proposed method for estimation of the apical bond length.

METHOD

Any two structures were compared by means of the root-mean-square deviation

$$\mathrm{rms}(\Delta X) = \left(\frac{1}{N} \sum_{i=1}^{N} (\Delta X_i)^2 \right)^{\frac{1}{2}} \tag{1}$$

where X denotes either the angles around copper (θ) or the apical bond length (b). Symbol Δ denotes the differences between the two structures. In this paper, two rms deviations were used: $\mathrm{rms}^{\mathrm{pl}}$ denotes the difference between the actual and the ideal square-planar structures as described by four *cis* (=90°) and two *trans* (=180°) angles, and rms (Δb) refers to the difference between the measured and the calculated apical bond lengths.

Deviation from planarity was also described by the difference between 360° and the sum of the four cis angles defining the position of the chelate ring (function A), and the sum of the trans angles subtracted from 360° (function B). The distortion vector $\boldsymbol{d}$ was defined as the sum of all the bond-vectors directed from the copper atom to the four ligand atoms of the chelate rings. This vector can be divided into two components: one dependent on the positions of the N atoms ($\boldsymbol{d}_N$) and the other defined by the positions of the O atoms ($\boldsymbol{d}_O$). The vector components in the -(Cu-OH$_2$) direction were denoted by *cd*(Cu-OW).

The results of molecular mechanics calculations and the description of the method and force fields (FF3'a, FF4'a and FF6'a) used are presented elsewhere.[13,14]

RESULTS AND DISCUSSION

According to the analysis of pentacoordinated phosphorous compounds,[15,16] the coordination polyhedron can be described by means of four regular bodies (Figure 1): two square pyramids (SP and SP') and two trigonal bipyramids (TP and TP'). All these coordination polyhedra have the C_2 axis passing through the Cu-OW bond in common (C_{2v} constraint). In addition, square pyramidal structures belong to the C_{4v} and trigonal bipyramidal structures to the C_{3h} representation (assuming the substituents to be equal).

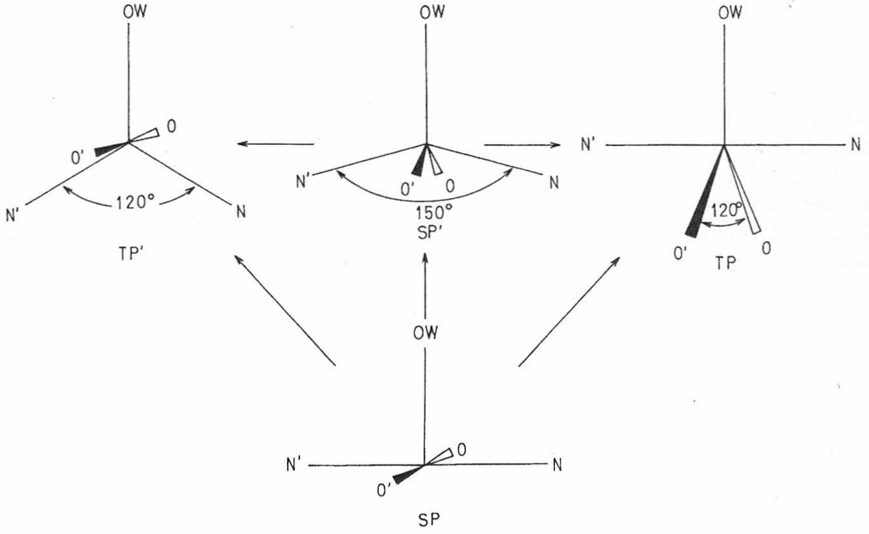

Figure 1. The four regular coordination polyhedra for coordination of copper(II) in chelates with *N*-alkylated amino acids: two square pyramids (SP and SP') and two trigonal bipyramids (TP and TP'). The Berry coordinate describes the distortion TP – SP' – TP'.

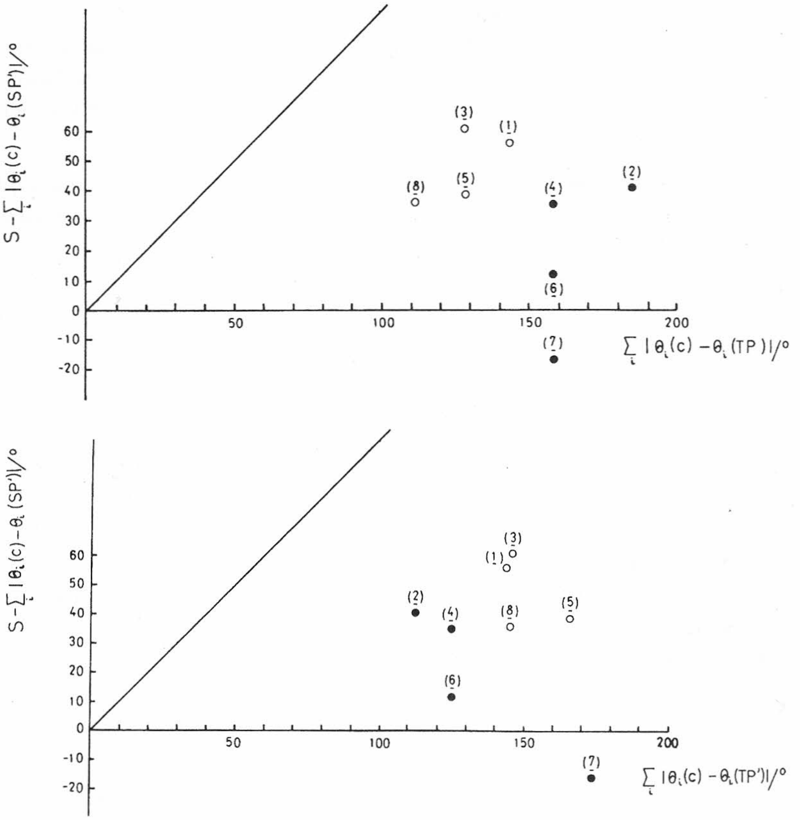

Figure 2. Plot of the distance of crystal structure (*c*) from square pyramid SP' *vs.* distances from (a) trigonal bipyramid TP and (b) trigonal bipyramid TP'. θ refers to any of ten valence angles defining copper coordination, and S (=136°) is the difference between SP' and TP (or TP'). The line with a slope = 1 is the Berry coordinate. Molecules: 1. aquabis(L-*N*,*N*-dimethylthreoninato)copper(II),[17] 2. aquabis(L-*N*,*N*-diethylalaninato)copper(II),[18] 3. aquabis(*N*,*N*-dimethylglycinato)copper(II),[19] 4. aquabis(L-*N*-benzylalaninato)copper(II),[12] 5. aquabis(L-*N*,*N*-dimethylisoleucinato)copper(II),[20] 6. aquabis(*N*-*tert*-butyl-*N*-methylglycinato)copper(II),[21] 7. diaquabis(D,L-prolinato)copper(II),[22] 8. aquabis(L-*N*,*N*-dimethylvalinato)copper(II).[14]

By plotting the distortion from the square pyramid SP' with respect to the distance from the trigonal pyramids TP and TP' (Figure 2), two groups of coordination polyhedra can be distinguished: the first includes molecules 1, 3, 5, 8 (group I) and the second molecules 2, 4, 6 and 7 (group II). The group I molecules are closer to the line with slope = 1 (Figure 2a), *i.e.* the Berry coordinate,[16] while the group II molecules are less distorted from the trigonal pyramid TP' (Figure 2b). The plot of the differences *vs.* the sum of trans angles (Figure 3) shows that distinction even more clearly: the group

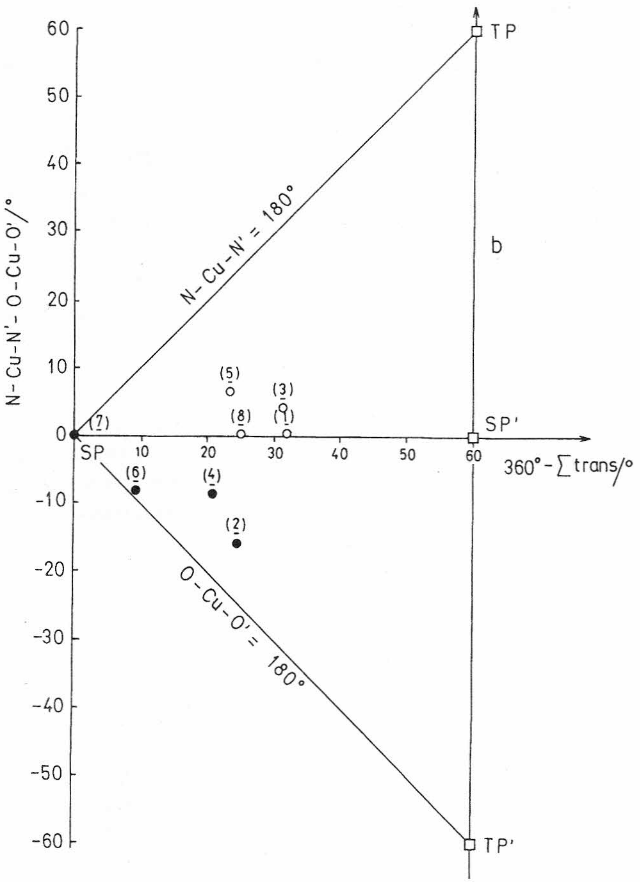

Figure 3. Plot of the difference of trans angles *vs.* their sum subtracted from 360° (function *A*): The Berry coordinate is denoted with *b*. For the numbering scheme of molecules, see Figure 2.

I molecules are distorted mainly in the SP – SP' direction with a slight distortion towards the bipyramid TP; in contrast, the group II molecules are distorted along the line O-Cu-O' = 180° towards the bipyramid TP'.

The two groups differ also in the values of the O-Cu-O' angles (162.3 to 167.56° for group I, 173.87 to 180° for group II). Needless to say, the compounds of the two groups also differ chemically: the first group consists of only *N,N*-dimethylated derivatives; the second consits of other *N*-alkylated as well as *N,N*-dialkylated deriatives (R = Me, Et, Bz, Bu^t).

Regressions of the apical bond length on distortion coordinates for all molecules (Table I) agree well with the previous results[13] on the same set of molecules, with the exception of **8** (N = 7); there are only slight differences in the slope and intercept values. All the regressions yielded a smaller S.E.

TABLE I

Linear regressions of the experimental Cu-OH_2 apical bond length on distortion coordinates[a]

No.	Coordinate	Group[b]	Slope (S.E.)c	Intercept(S.E.)[c]	*r*	*p*
1	$\mathrm{rms}^{\mathrm{Pl}}$	I	–0.1020(0.0234)	3.2712(0.2208)	–0.951	0.0487
2		II	–0.0593(0.0255)	2.8221(0.1930)	–0.855	0.1452
3		both	–0.0557(0.0142)	2.8155(0.1216)	–0.848	0.0078
4	A	I	–0.0846(0.0297)	2.5942(0.1030)	–0.896	0.1044
5		II	–0.1095(0.0201)	2.4832(0.0271)	–0.968	0.0322
6		both	–0.0556(0.0166)	2.4656(0.0436)	–0.808	0.0153
7	B	I	–0.0199(0.0074)	2.8631(0.2065)	–0.886	0.1143
8		II	–0.0114(0.0014)	2.5366(0.0229)	–0.986	0.0143
9		both	–0.0089(0.0022)	2.5315(0.0501)	–0.859	0.0063
10	A + B	I	–0.0161(0.0059)	2.8120(0.1858)	–0.888	0.1124
11		II	–0.0104(0.0011)	2.5333(0.0190)	–0.990	0.0102
12		both	–0.0078(0.0019)	2.5249(0.0488)	–0.858	0.0064
13	180 – N-Cu-N'	I	–0.0308(0.0006)	2.6956(0.0079)	–1.000	0.0004
14		II	–0.0143(0.0032)	2.5362(0.0415)	–0.954	0.0460
15		both	–0.0169(0.0032)	2.5438(0.0413)	–0.908	0.0018
16	180 – O-Cu-O'	I	–0.0147(0.0306)	2.5355(0.4713)	–0.321	0.6791
17		II	–0.0410(0.0102)	2.4967(0.0387)	–0.943	0.0571
18		both	–0.0087(0.0055)	2.4257(0.0615)	–0.543	0.1639
19	**d**	I	–0.5539(0.2028)	2.8433(0.1968)	–0.888	0.1120
20		II	–0.3207(0.0324)	2.5328(0.0188)	–0.990	0.0101
21		both	–0.2563(0.0601)	2.5301(0.0481)	–0.867	0.0053
22	*cd*(Cu-OW)	I	–0.1649(0.0389)	2.4319(0.0345)	–0.949	0.0514
23		II	–0.3213(0.0333)	2.5327(0.0193)	–0.990	0.0105
24		both	–0.2191(0.0356)	2.4783(0.0267)	–0.929	0.0008
25	cd_{N}(Cu-OW)	I	–0.8411(0.0143)	2.6843(0.0065)	–1.000	0.0003
26		II	–0.3975(0.0964)	2.5349(0.0449)	–0.946	0.0541
27		both	–0.4727(0.0907)	2.5424(0.0418)	–0.905	0.0020
28	cd_{O}(Cu-OW)	I	–0.4126(0.8325)	2.5231(0.4308)	–0.331	0.6693
29		II	–1.0665(0.3189)	2.4721(0.0407)	–0.921	0.0790
30		both	–0.2561(0.1569)	2.4235(0.0591)	–0.555	0.1537

[a] Lengths are expressed in Å and angles in degrees. For definition of distortion coordinates, see the Method section.

[b] Group I: **1**, **3**, **5**, **8**; Group II: **2**, **4**, **6**, **7** (see caption to Figure 2)

[c] S.E., standard error.

value for both slope and intercept, smaller *p* and bigger |*r*|, with the exception for the latter in regressions 15, 24 and 27. Again, the best results were obtained by correlating the components of distortion vectors in the -(Cu-OW) direction and angle N-Cu-N' (regressions 24, 27 and 15). The poorest results were obtained with the variables dependent exclusively on the position of O atoms (regressions 18 and 30).

Comparison of regressions done on separate groups shows that group II yielded generally better results in terms of the regression coefficient. This might be due to the fact that, when distortion was described with the position of both nitrogen and oxygen atoms, group II yielded better regression lines (compare regressions 4 with 5, 7 with 8, 11 with 12, 19 with 20, and 22 with 23). However, when the distortion coordinate was dependent only on the position of O atoms (regressions 16 and 17, 28 and 20), the value of r was very much in favour of group II. The opposite is true of the coordinates dependent only on the position of N atoms, that is N-Cu-N' and cd_N(Cu-OW), but the difference in r between groups I and II is not so strongly pronounced (*cf.* regressions 13 and 14; 25 and 26). Obviously, due to the greater dependence of the apical bond length on the position of N atoms, the best results were obtained for group I (r = –0.9996 for regression 13, r = –0.9997 for regression 25); the best results for group II were not so good (r = 0.990 for regresions 11, 20 and 23). The regression lines differ considerably for variables dependent only on the position of one kind of atoms; there is a difference in the slope up to factor 2.8 (regressions 13 and 14; 16 and 17; 25 and 26; 28 and 29), but the differences between the intercepts in these regressions are not higher than usual (*cf.* 0.15 Å for regressions 25 and 26, 0.45 Å for regressions 1 and 2). The most characteristic regression lines are presented in Figure 4.

A very high correlation of the apical bond length on the N-Cu-N' angle in »square pyramids« (*i.e.* group I molecules) led to the conclusion that the »missing variable« was not the O-Cu-O' angle itself (as it was supposed in ref. 13), but rather the difference between two trans angles, *i.e.* distortion from the pseudo C_{4v} structure. Taking the difference between two trans angles (regression 31, Table II) as a second variable, better agreement was obtained in terms of regression coefficients (*cf.* regressions 15 and 31), but the

TABLE II

Multiple linear regression of the experimental (Cu-OH_2) bond lengths on distortion coordinates (N = 8)[a]

No.	Coordinate	Regression coefficient (S.E.)[b]	Regression constant (S.E.)b	|R|
31	180 – N-Cu-N' N-Cu-N' – O-Cu-O'	–0.01911(0.00334) –0.00385(0.00273)	2.55930(0.03981)	0.935
32	180 – N-Cu-N' |N-Cu-N' – O-Cu-O'|	–0.02089(0.00188) 0.00887(0.00210)	2.54208(0.02114)	0.981
33	180 – N-Cu-N' (N-Cu-N' – O-Cu-O')^2	–0.02114(0.00252) 0.00056(0.00019)	2.56189(0.02776)	0.968

[a] All lengths are expressed in Å and angles in degrees.

[b] S.E., standard error.

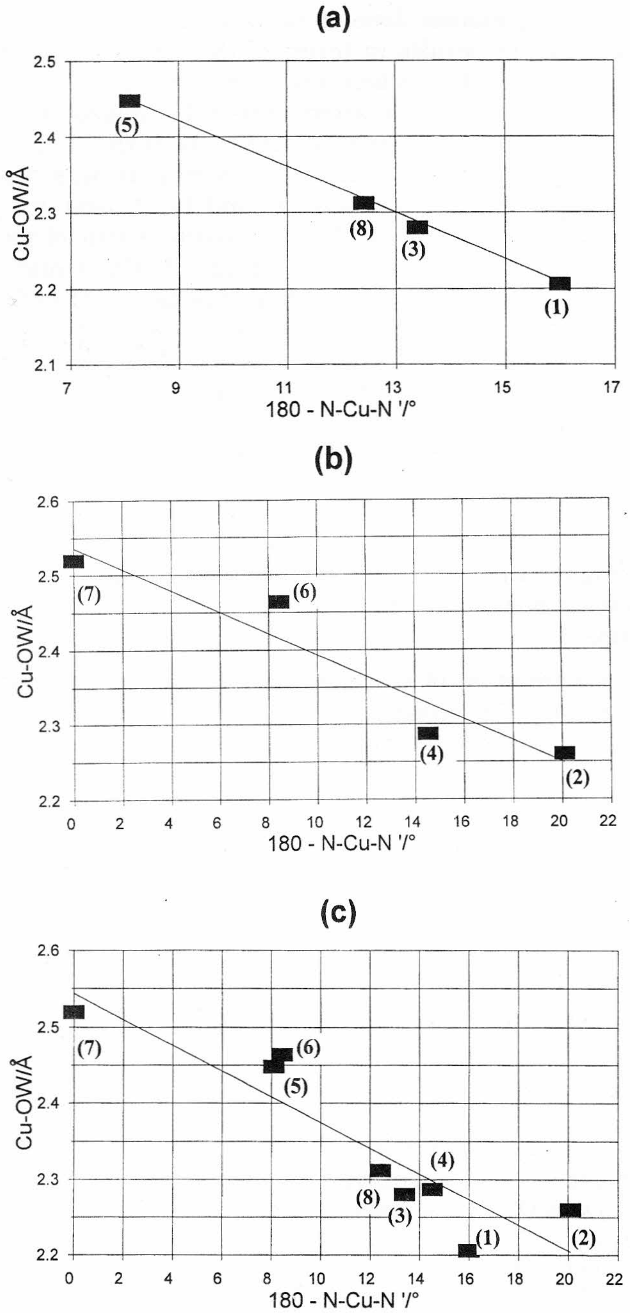

Figure 4. Regression lines for (a) group I (regression 13, Table I), (b) group II (regression 14) and (c) both groups (regression 15). For the numbering scheme, see caption to Figure 2.

ratio between S.E. and regression coefficient to the second variable was as high as 0.71. (It has to be noted that regression 31 is equivalent to the regression on the N-Cu-N' and O-Cu-O' coordinates referred to in[13]). By using the regression on *absolute* differences between two trans angles (regression 32), the S. E./coefficient ratio dropped to 0.24 and $|R|$ rose to 0.981. The significance level for the regression coefficient of the second variable changed from the unacceptably high value of 0.218 (regression 31) to only 0.008 (regression 32). This is the best result obtained so far for both groups of molecules, and no improvement was obtained by correlating the bond lengths on the square of the differences between trans angles (regression 33).

For estimation of the apical bond length, two regression lines with lowest S.E./slope ratios for group I molecules (regression 13) and group II molecules (regression 14) were chosen (Table III). The regression with the highest $|R|$ values (32) was also checked and, among the few force fields for molecular mechanics calculations,[13,20] the three most characteristic (FF3'a, FF4'a, FF6'a) were chosen. All regression functions and force fields gave higher values for the mean apical bond length ($\bar{b}$) than those observed experimentally for both groups taken separately or together, except in three cases. The root-mean-square deviation between the calculated and the estimated bond lenghts varies in the high range from 0.032 to 0.300 Å, but substantially better results were obtained for groups II (rms(Δb) = 0.032 – 0.086 Å) than for group I (rms(Δb) = 0.083–0.300 Å). The best agreement between experiment and theory for both groups taken together rms(Δb) = 0.068 Å is better than the best value for the root-mean-square deviation (0.080 Å) reported previously.[13]

Such a discrepancy between theory and experiment is mainly due to the poor reproduction of the shape of the coordination polyhedron by means of molecular mechanicas calculations rather than to bad regression functions. The maximum distance of the experimental point (**1** and **3**) in regression 13 from the regression line in the Cu-OH_2 direction is only 0.003 Å, but that regression did not give the best agreement between experiment and theory. Also, generally smaller rms(Δb) values were obtained from regressions on all molecules taken together than on the groups taken separately.

Dependence of the reproduction of the apical bond length on the shape of the coordination polyhedron is visible from the fact that all force fields did not yield the same agreement between theory and experiment. The best results for all three regressions were obtained with force field FF6'a, which is possibly due to the fact that that force field was fitted to reproduce the N-Cu-N' angle as well as possible.[13]

Therefore, the reason why the group I molecules yielded generally poorer results than those of group II can be easily found in the poorer reproduction of copper coordination. The systematically higher value for the apical bond length of **1** ($\bar{b}_{\text{calc.}}$ = 2.418(0.053 S.D.) Å, *cf.* $\bar{b}_{\text{meas.}}$ = 2.206(3) Å is obviously due to the poor reproduction of the N-Cu-N' angle (meas. 164.0(2), calc. 170.9 – 173.0°).[13,17] Molecules that yielded the best reproduction of the N-

TABLE III

Measured crystal structures (experimental data) (CR) and estimated apical bond lengths (Å) from the functions obtained from linear regressions (Tables I and II)[a]

Comp.	CR	Regressions no. 13(I), 14(II), 15(both)					
		FF3'a		FF4'a		FF6'a	
		I(II)	both	I(II)	both	I(II)	both
1	2.206(3)	2.480	2.425	2.468	2.419	2.415	2.390
2	2.260(4)	2.297	2.260	2.311	2.276	2.280	2.239
3	2.28 (2)	2.459	2.414	2.459	2.414	2.351	2.354
4	2.287(2)	2.376	2.353	2.390	2.370	2.318	2.285
5	2.448(6)	2.425	2.395	2.425	2.395	2.305	2.329
6	2.464(2)	2.527	2.533	2.525	2.530	2.524	2.530
7	2.52	2.536	2.544	2.536	2.544	2.536	2.544
8	2.312(2)	2.400	2.381	2.395	2.378	2.332	2.344
$\bar{b}$		2.441(I)	2.413	2.437(I)	2.416	2.351(I)	2.377
		2.434(II)		2.441(II)		2.415(II)	
rms(Δb)		0.170(I)	0.136(I)	0.164(I)	0.133(I)	0.132(I)	0.117(I)
		0.058(II)	0.049(II)	0.066(II)	0.055(II)	0.036(II)	0.037(II)
			0.102		0.102		0.087

Comp.	CR	Regressions no. 10(I), 11(II), 12(both)					
		FF3'a		FF4'a		FF6'a	
		I(II)	both	I(II)	both	I(II)	both
1	2.206(3)	2.468	2.358	2.514	2.381	2.365	2.308
2	2.260(4)	2.299	2.349	2.309	2.356	2.276	2.332
3	2.28 (2)	2.603	2.423	2.697	2.435	2.513	2.380
4	2.287(2)	2.264	2.323	2.323	2.368	2.139	2.229
5	2.448(6)	2.587	2.416	2.608	2.426	2.511	2.379
6	2.464(2)	2.420	2.440	2.427	2.445	2.398	2.424
7	2.52	2.533	2.525	2.533	2.525	2.533	2.525
8	2.312(2)	2.560	2.403	2.566	2.406	2.469	2.358
$\bar{b}$		2.555(I)	2.405	2.596(I)	2.418	2.465(I)	2.368
		2.379(II)		2.398(II)		2.337(II)	
rms(Δb)		0.252(I)	0.115(I)	0.300(I)	0.126(I)	0.164(I)	0.083(I)
		0.032(II)	0.050(II)	0.036(II)	0.052(II)	0.082(II)	0.050(II)
			0.089		0.100		0.068

Cu-N' angle (theor. 164.68° (FF6'a), exp. 165.47(9)° for **4**;[12,13] theor. 171.2° (FF3'a), exp. 171.9(2)° for **5**[13,20] yielded also the best values fore the apical bond length (2.285 Å for **4**, regression 15; 2.425 Å for **5**, regression 13).

TABLE III

(continuing)

Comp.	CR	Regression no. 32		
		FF3'a	FF4'a	FF6'a
1	2.206(3)	2.447	2.410	2.415
2	2.260(4)	2.268	2.283	2.238
3	2.28 (2)	2.408	2.419	2.352
4	2.287(2)	2.315	2.344	2.245
5	2.448(6)	2.396	2.406	2.346
6	2.464(2)	2.615	2.603	2.627
7	2.52	2.542	2.542	2.542
8	2.312(2)	2.364	2.368	2.297
$\bar{b}$		2.404(I)	2.401(I)	2.353(I)
		2.435(II)	2.443(II)	2.413(II)
		2.419	2.442	2.383
rms(Δb)		0.141(I)	0.128(I)	0.122(I)
		0.078(II)	0.077(II)	0.086(II)
		0.114	0.106	0.105

[a] I and II refer to groups defined in Table I.

In spite of the fact that further improvement of the method has to be primarily viewed in the development of molecular mechanics models for a better reproduction of copper(II) coordination, it has to be noted that the best apical bond length reproduction (rms (ΔCu-OW) = 0.032 Å) reaches the limit of reproduction of other copper-to-ligand bonds (rms(ΔCu-O) = 0.029 Å, rms(ΔCu-N) = 0.027 Å; group I, FF3'a).[14,17,19,20] Unfortunately, the paucity of experimental data does not permit going into a deeper analysis of the proposed method.

Acknowledgment. – The author thanks Mrs. D. Šimić for assistance with the regression analysis.

REFERENCES

1. N. Paulić and N. Raos, *J. Coord. Chem.* **31** (1994) 181.
2. A. B. Corradi, *Coord. Chem. Rev.* **117** (1992) 45.
3. V. A. Davankov, S. V. Rogozhin, A. A. Kurganov, and L. Ya. Zhuchkova, *J. Inorg. Nucl. Chem.* **37** (1975) 369.
4. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **56** (1983) 79.
5. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **57** (1984) 1217.
6. V. A. Davankov and A. V. Semechkin, *J. Chromatogr.* **141** (1977) 313.
7. B. Kaitner, B. Kamenar, N. Paulić, N. Raos, and Vl. Simeon, *J. Coord. Chem.* **15** (1987) 373.

8. J. Sabolović, N. Raos, and Kj. Rasmussen, *Croat. Chem. Acta* **62** (1989) 495.
9. J. Sabolović and N. Raos, *Polyhedron* **9** (1990) 1277.
10. J. Sabolović, *Polyhedron* **12** (1993) 1107.
11. J. Sabolović and Kj. Rasmussen, *Inorg. Chem.* **34** (1995) 1221.
12. B. Kaitner, E. Meštrović, N. Paulić, and N. Raos, *J. Coord. Chem.* **34** (1995) 55.
13. N. Raos, *J. Mol. Struct.* **355** (1995) 211.
14. B. Kaitner, G. Pavlović, N. Paulić, and N. Raos, *J. Coord. Chem.* **36** (1995) 327.
15. R. S. Berry, *J. Chem. Phys.* **32** (1960) 933.
16. R. R. Holmes and J. A. Deiters, *J. Amer. Chem. Soc.* **99** (1977) 3318.
17. B. Kaitner, G. Ferguson, N. Paulić, and N. Raos, *J. Coord. Chem.* **30** (1993) 233.
18. B. Kaitner, N. Paulić, and N. Raos, *J. Coord. Chem.* **25** (1992) 337.
19. T. S. Cameron, K. Prout, F. J. C. Rossotti, and D. Steele, *J. Chem. Soc. Dalton Trans.* (1973) 2626.
20. B. Kamenar, M. Penavić, A. Škorić, N. Paulić, N. Raos, and Vl. Simeon, *J. Coord. Chem.* **17** (1988) 85.
21. B. Kaitner, G. Ferguson, N. Paulić, and N. Raos, *J. Coord. Chem.* **26** (1992) 95.
20. A. McL. Mathieson and H. K. Welsh, *Acta Crystallogr.* **5** (1952) 599.

SAŽETAK

Analiza oblika koordinacijskog poliedra pentakoordiniranih bakrovih(II) kelata s *N*-alkiliranim aminokiselinama

Nenad Raos

Analiza osam pentakoordiniranih akvabakrovih(II) kelata s *N*-alkiliranim aminokiselinama pokazala je da se oni mogu prema obliku koordinacijskog poliedra podijeliti u dvije skupine. Poliedri prve skupine, koju sačinjavaju *N,N*-dimetilirani derivati, mogu se opisati kao distordirane kvadratne piramide s pseudo-simetrijom C_{4v}. Poliedri pak druge skupine, koju sačinjavaju ostali *N*-alkilirani i *N,N*-dialkilirani derivati, mogu se opisati kao kvadratne piramide distortine prema trigonskoj bipiramidi uzduž osi O-Cu-O' = 180°. Duljina apikalne veze (Cu-OH_2) izuzetno je dobro korelirana s kutom N-Cu-N' ($r = 0.9996$) za prvu skupinu molekula i osjetno slabije za drugu skupinu ($r = 0.954$). Višestruka regresija eksperimentalne duljine apikalne veze s obzirom na kut N-Cu-N' i apsolutnu razliku kutova |N-Cu-N' – O-Cu-O'| dala je $|R| = 0.981$ za $N = 8$. Opisujući oblik bakrova koordinacijskog poliedra različitim mjerama distorzije, bilo je moguće predvidjeti duljinu apikalne veze iz struktura dobivenih molekulsko-mehaničkim proračunom s minimalnom vrijednošću korijena srednjega kvadratnog odstupanja eksperimentalne od teorijske vrijednosti u iznosu od 0.083 Å (skupina I), 0.032 Å (skupina II) i 0.068 Å (sve molekule).