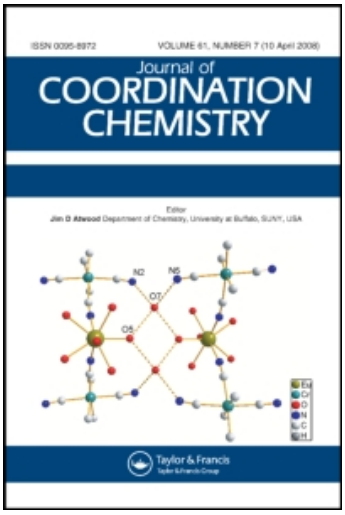


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

REVIEW: THE CHEMISTRY OF CHELATES WITH *N*-ALKYLATED AMINO ACIDS

N. Paulić[a]; N. Raos[a]
[a] Laboratory for Analytical and Physical Chemistry, Institute for Medical Research and Occupational, Health, University of Zagreb, Zagreb, Croatia

To cite this Article Paulić, N. and Raos, N.(1994) 'REVIEW: THE CHEMISTRY OF CHELATES WITH *N*-ALKYLATED AMINO ACIDS', Journal of Coordination Chemistry, 31: 3, 181 — 190
To link to this Article: DOI: 10.1080/00958979408024214
URL: http://dx.doi.org/10.1080/00958979408024214

J. Coord. Chem., 1994, Vol 31, pp. 181–190
Reprints available directly from the publisher
Photocopying permitted by license only

REVIEW

THE CHEMISTRY OF CHELATES WITH *N*-ALKYLATED AMINO ACIDS

N. PAULIĆ and N. RAOS*

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

(Received August 2, 1993)

N-alkylated α-amino acids are compounds very suitable for studying steric effects in chelates with heavy metals, especially copper(II). These chelates are especially interesting because of pronounced stereoselective effects (enantioselectivity) as well as because of distortion of the copper coordination polyhedron. In this short review all the aspects of coordination chemistry of *N*-alkylated amino acids are presented and steric effects are discussed from the viewpoint of results obtained from X-ray analyses and molecular mechanics calculations.

KEYWORDS: *N*-alkylaminoacids, copper(II), structures, conformation, stereochemistry, molecular mechanics, review

INTRODUCTION

Interest in complexes of *N*-alkylated amino acids (mostly copper(II) chelates) is closely related to the enantioselectivity effect observed in that class of compounds. From two enantiomeric ligands (*L* and *D*), three bis-complexes can be formed: optically active species (MLL and MDD) and a *meso* chelate (MLD). The relation (*1*)

$$\alpha = \frac{[\mathrm{MLD}]}{[\mathrm{MLL}] + [\mathrm{MDD}]} \qquad (1)$$

gives the degree of enantioselectivity and is connected with the difference in Gibbs energy between *meso* and racemic complexes, (*2*)

$$\Delta\Delta G^0 = \Delta G^0_{DL} - \Delta G^0_{rac} = -RT \ln \alpha \qquad (2)$$

Interesting to note, the enantioselectivity effect was not observed in chelates with naturally occurring amino acids. A difference in energy between racemic and *meso* complexes was not observed in copper(II) complexes with alanine, phenylalanine,

* Author for correspondence.

valine and proline.[1] In this laboratory we tried to observe the enantioselectivity effect in complexes of alanine and phenylalanine with heavy metals (Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+}) but without success.[2] Measurements of the heat of reaction of copper, nickel and zinc complexes with alanine, valine and proline also confirmed the previously obtained results.[3]

Contrary to naturally occurring amino acids, their *N*-alkylated and *N,N*-dialkylated derivatives show a very pronounced enantioselectivity effect in aqueous solution and solutions of organic liquids (Table 1). In fact, the enantioselectivity effect in that class of compounds was first observed for *N*-benzylproline.[4] The phenomenon was later used for designing resins for ligand exchange chromatography.[5]

Enantioselectivity in non-aqueous solutions, with the solute incapable of coordination, can be attributed to interactions of bulky side chains which destabilize the optically active complexes. (see Scheme 1). Molecular mechanics calculations revealed that the *trans* configuration is energetically favourable owing to steric interactions of *N,N*-dimethyl groups in a *cis* configuration (around 10 kJ mol^{-1} for *N,N*-dimethylalanine).[6] The *trans* configuration of these compounds was also confirmed by *e.s.r.* measurements.[7]

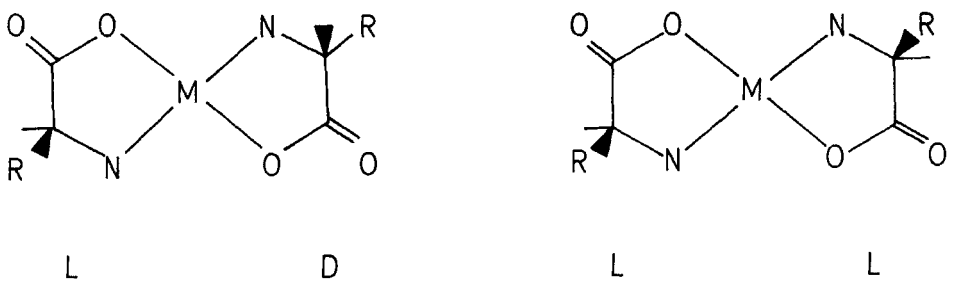


Table 1 Enantioselectivity effect ($\Delta\Delta G^0$, Eq. (2)) in complexes of *N*-alkylated amino acids.

Ligand	Solvent			Reference
	H_2O	CH_3OH	$CHCl_3$	
N,N-dimethylalanine	0.0			34
N-benzylalanine	>0.0			34
N-methyl-*N*-benzylalanine	3.13	-0.57	-3.13	34
N-methylvaline	0.0			34
N,N-dimethylvaline	0.0	-0.57(0.0)*	3.42(3.49)*	34
N-benzylvaline		-1.44		34
N-methyl-*N*-benzylvaline	>0.0	-0.57	3.13	34
N,N-dimethylisoleucine	<0.0	0.29*	3.70*	34
N-benzylisoleucine		-1.14		34
N-methylproline	0.0			34
N-benzylproline	5.12	2.27(3.99)*	3.42(4.55)*	34
	4.89			4
	4.00			35
N-benzyl-4-hydroxy-*allo*-proline	0.91			36

* Calculated from CD spectra; the other constants were obtained by means of potentiometrictitrations.

PREPARATION OF COMPLEXES

The most convenient synthesis of *N*-alkylated amino acids involves reaction of amino acids with an aldehyde and subsequent hydrogenation on Pd/C (Stroud-Bowman method),[8] (*3*).

$$H_2N\text{-}CH(R_1)\text{-}COOH \xrightarrow[2\,RCHO]{2\,H_2/Pd} (R)_2N\text{-}CH(R_1)\text{-}COOH \qquad (3)$$

The second method (used for benzylation) involves reaction with sodium borhydride,[9] (*4*).

$$H_2N\text{-}CH(R)\text{-}COOH \xrightarrow[C_6H_5CHO]{NaBH_4} C_6H_5CH_2NH\text{-}CH(R)\text{-}COOH \qquad (4)$$

For the synthesis of *N-tert*-butyl derivatives, neither reaction is applicable. *N-tert*-butylglycine was prepared by means of the reaction[10] (*5*).

$$(CH_3)_3C\text{-}NH_2 + BrCH_2COOC_2H_5 \xrightarrow{-HBr} (CH_3)C\text{-}NH\text{-}CH_2COOC_2H_5 \qquad (5)$$

The product obtained is hydrolysed with NaOH, and treated with acid to form the amino acid. The copper(II) complexes can be prepared by reaction of the sodium salt of the ligand with copper acetate monohydrate[11] or with fresh copper hydroxyde and acidic form of the ligand.[12]

COMPLEX FORMATION AND STABILITY

The influence of *N*-alkylation of the amino acids on the stability of copper(II) and nickel(II) chelates was first systematically studied by Basolo and Chen.[13] They prepared seven glycine derivatives: five monosubstituted (methyl, ethyl, *n*-propyl, *n*-butyl and *i*-propyl) and two disubstituted ones (*N,N*-dimethylglycine and *N,N*-diethylglycine). The pK_{COOH} values for all *N*-alkylglycines were approximately the same as was to be expected (Table 2).

It is also evident that the chelating tendency of the *N*-alkylglycines is less pronounced than that of glycine. The tendency drops through the methyl to the ethyl derivative after which it virtually levels off through the *N-n*-butyl derivatives.

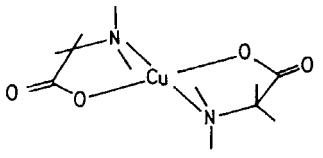
Table 2 Stability constants of chelates with *N*-alkylated glycine.*

			Copper(II)		Nickel(II)	
Ligand	pK_1	pK_2	β_{110}	β_{120}	β_{110}	β_{120}
Gly	2.43	9.62	8.38	15.17	5.86	10.64
MeGly	2.24	10.01	7.94	14.59	5.50	9.88
EtGly	2.30	10.10	7.34	13.55	4.81	8.54
n-PrGly	2.28	10.03	7.25	13.31	4.79	8.46
n-BuGly	2.29	10.07	7.32	13.52	4.76	8.38
i-PrGly	2.36	10.06	6.70	12.45	3.94	
Me_2Gly	2.08	9.80	7.30	13.65	4.82	8.60
Et_2Gly	2.04	10.47	6.88	12.86	4.21	

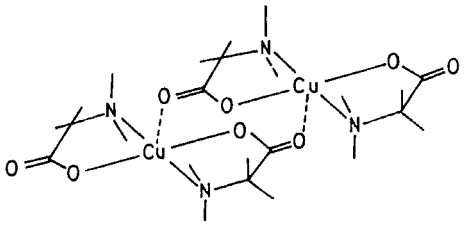
* Taken from ref. 13.

The most bulky group, isopropyl, gives rise to the maximum steric effects of all compounds studied.

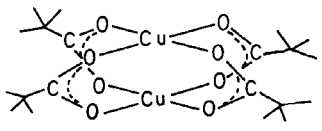
The problem of complex stability is not easy to solve because copper(II) chelates with *N*-alkylated amino acid exist in various chemical forms. Rogozhin and co-workers[14] carried out spectroscopic measurements on *N*-benzyl, *N,N*-dibenzyl and *N,N*-dimethyl derivatives of proline, leucine and valine in various solvents (water, water/methanol mixtures, chloroform and dioxan). They found that complexes of *N*-alkylated amino acids could exist in the form of a distorted octahedral (blue, II), a square planar (red, I) and a green, binuclear "acetato like" structure (III, see Scheme 2). Complexes may exist also in the form of aqua-complexes (blue modification).



I

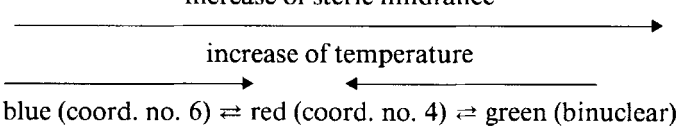


II



III

According to Rogozhin and coworkers,[14] the octahedral complex has a chelate ring coordinated in the plane (in *trans*-position) and an apically bound molecule of solvent (water or methanol). Nash and Schaefer[11] found that copper(II) chelates with *N,N*-dialkyl-α-amino acids in non-polar solvents formed complexes with coordination number 4, but also that they could (by association) form complexes with coordination number 6 by cooling the solutions. The following scheme describes the tendency to form three modifications:



Binding of a water molecule to the apical position (blue modification) is closely connected with the enantioselectivity effect in aqueous solution (Table 1). Studying stereoselectivity in the *N*-benzylvaline system, Davankov[15] found by various methods (ligand-exchange chromatography, polarimetric titration, electronic spectroscopy and X-ray analysis) that in aqueous and methanolic solutions CuLL (or CuDD) complexes are more stable than *meso* chelates because only these structures

could, because of steric reasons, bind a water or a methanol molecule in the apical position. For the same reason the *meso* complexes of *N*-benzylproline were more stable than the optically active complexes. Therefore, it was concluded that the structure was more stable if additional ligation of the solute molecule in the apical position took place.

CRYSTAL STRUCTURES

Copper(II) chelates with *N*-alkylated α-amino acids appear in two kinds of complexes: aqua-complexes with apically bound ligand water (blue modification) and complexes without ligand water (red modification; Figs. 1 and 2).

Angles around the central atom (Table 3) reveal that both kinds of complexes generally form distorted coordination polyhedra. Obviously, this is due to steric interactions between bulky substituents on nitrogen atom, side chains of amino acids and, in the case of aqua-complexes, interactions with ligand water.

Values from Table 3 yield mean Cu-O distances for aqua-complexes (1.931 Å) longer than the Cu-O distance for the red modification (1.904 Å). The same trend is observed for Cu-N distances (2.055 and 2.022 Å for blue and red modifications, respectively) but the trends do not appear to be statistically significant. The *trans*-angles (N-Cu-N and O-Cu-O) vary from strictly planar coordination (180°) to highly distorted (161.5° for the complex with *N,N*-dimethylvaline). The intra-anular *cis*-angles around copper are smaller (mean 84.7°) than the inter-anular ones (mean 94.7°). These values do not appear to vary with the distortion of the coordination polyhedron.

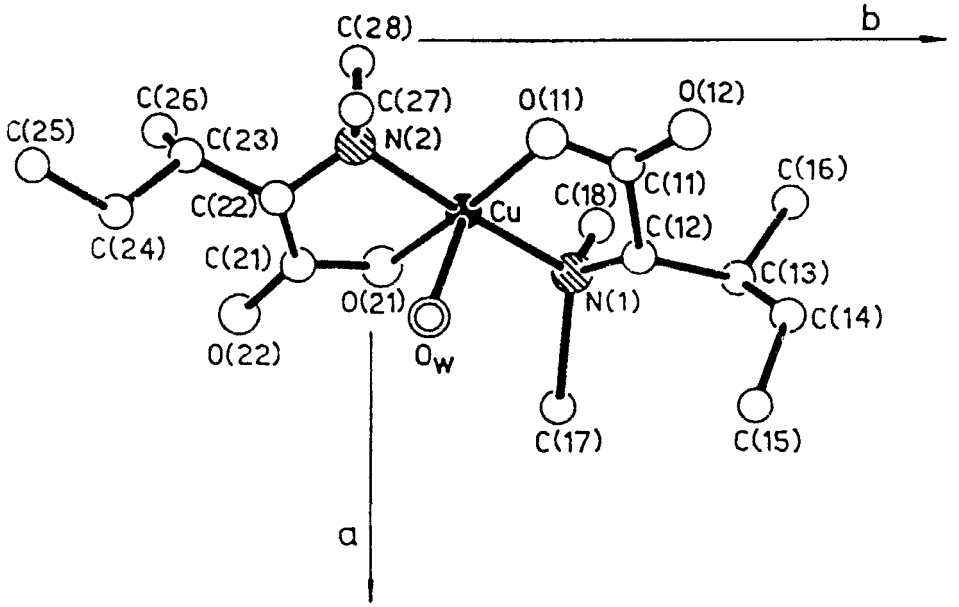


Figure 1 The structure of aqua*bis*(*L-N,N*-dimethylisoleucinato)copper(II). Taken from ref. 39.

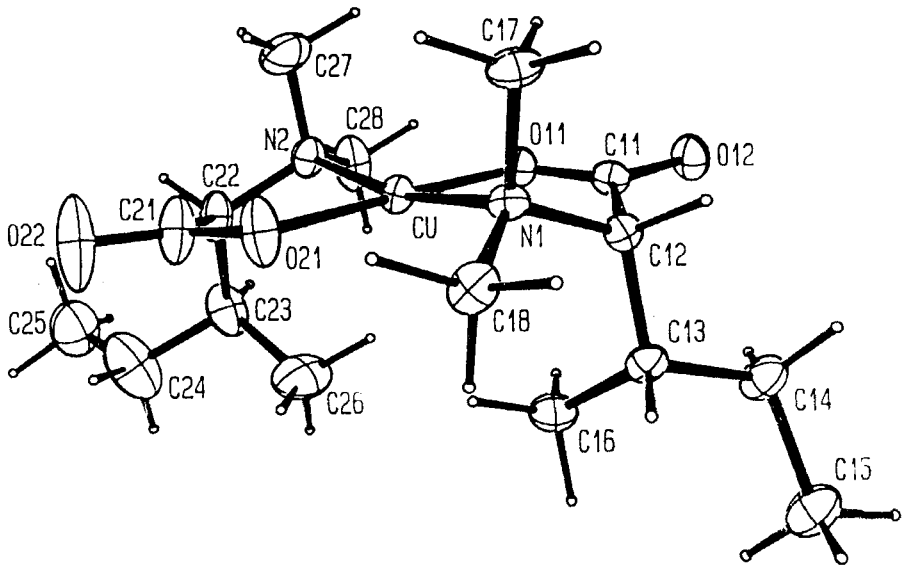


Figure 2 Red modification of *bis*(*L*-*N*,*N*-dimethylisoleucinato)copper(II). Taken from ref. 40.

CONFORMATIONAL ANALYSIS

Copper(II) complexes with *N*,*N*-dialkylated amino acids are very interesting for conformational analysis by means of molecular mechanics methods.[16–19] The chelates are soluble in solutions incapable of coordination (e.g. chloroform) from which crystals of the red modification suitable for X-ray analysis can be obtained. The crystal structure of the red modification can be treated by using the *in vacuo* approximation in molecular mechanics, *i.e.*, neglecting intermolecular interactions. The approximation holds true because molecules lack a specific intermolecular interaction (*e.g.*, hydrogen bonding with amine hydrogen atoms or additional apical coordination with the neighbouring molecules).

Results of molecular mechanics calculations have to answer a few specific questions. A copper(II) chelate with an alkylated amino acid can exist in numerous conformations (as many as several hundreds). Molecular mechanics calculations aim to find the most stable conformation (*i.e.*, the one with the lowest strain energy) and to ascertain whether this conformation corresponds to the conformation found in the crystal state. If not, results suggest the existence of intermolecular interactions which are not (*in vacuo* approximation) calculated.

The difference in average Gibbs energy* between two diastereomers (MLL and MLD complexes) corresponds to the enantioselectivity effect (*2*) in a solvent incapable of coordination. Because of the vicinity of bulky groups in the two chelate

* Defined as $\langle G \rangle = \frac{\Sigma_i G_i \exp(G_i/RT)}{\Sigma_j \exp(G_j/RT)}$ where G_i (or G_j) are conformational energies of conformers.

Table 3 Comparison of crystal geometry for copper(II) coordination of complexes with *N*-alkylated amino acids.*

Compound	Cu-O	Cu-O′	Cu-N	Cu-N′	O-Cu-O′	N-Cu-N′	N′-Cu-O′	N′-Cu-O	N-Cu-O′	N-Cu-O	Re
$Me_2Val)_2Cu$, LL	1.896(2)	1.902(2)	2.022(2)	2.026(3)	175.7(1)	161.5(1)	84.3(1)	97.2(1)	95.3(1)	84.5(1)	28
$Me_2Ile)_2Cu\text{-}H_2O$, LL	1.900(5)	1.949(5)	2.014(5)	2.019(5)	165.1(5)	171.9(2)	83.4(2)	95.2(2)	95.1(2)	84.1(2)	39
$Me_2Ile)_2Cu$, LL	1.911(4)	1.886(5)	2.009(4)	2.007(4)	178.3(2)	166.0(2)	83.9(2)	96.3(2)	95.8(2)	84.4(2)	40
$Et_2Ala)_2Cu$, DL	1.910(2)	1.910(2)	2.033(2)	2.033(2)	180.0	180.0	84.1(1)	95.9(1)	95.9(1)	84.1(1)	29
$Et_2Ala)_2Cu\text{-}H_2O$, LL	1.922(2)	1.922(2)	2.075(4)	2.075(4)	175.6(1)	159.9(2)	83.4(2)	95.5(2)	95.5(2)	83.4(2)	30
$Bu^tMeGly)_2Cu\text{-}H_2O$	1.922(2)	1.922(2)	2.081(2)	2.081(2)	179.40(8)	171.55(8)	84.85(7)	95.19(7)	95.19(7)	84.85(7)	31
$Bu^tBzGly)_2Cu$	1.874(2)	1.874(2)	2.112(3)	2.112(3)	180.0	180.0	85.4(1)	94.6(1)	94.6(1)	85.4(1)	32
$Me_2Thr)_2Cu\text{-}H_2O$, LL	1.930(3)	1.926(3)	2.042(3)	2.055(3)	163.9(2)	164.0(2)	82.9(1)	95.8(1)	94.0(1)	82.9(1)	33
$BzVal)_2Cu\text{-}H_2O$, DL	1.94(2)	1.90(2)	2.04(2)	2.08(2)	180(1)	163(1)	86(1)	96(1)	93(1)	84(1)	15
$BzVal)_2Cu$, DL	1.933(8)	1.933(8)	1.997(9)	1.997(9)	180.0	180.0	85.0(3)	95.0	95.0	85.0(3)	41
$Me_2Gly)_2Cu\text{-}H_2O$	1.97(2)	1.97(2)	2.04(2)	2.06(2)	162.3(8)	166.6(8)	85.1(8)	92.6(7)	93.9(9)	84.3(8)	36
$BzPro)_2Cu$, DL	1.95(2)	1.95(2)	1.92(2)	1.92(2)	180	180	88	92	92	88	37
$BzPro)_2Cu$, LL	1.87(2)	1.85(1)	2.09(2)	2.04(2)			86(1)	93(1)	95(1)	86(1)	38

*The bond lengths are expressed in Å, bond angles in °.

rings, much distortion of the coordination polyhedron takes place (see Table 3). This phenomenon led us to develop novel molecular mechanics models suitable for calculating distortions of the copper(II) coordination polyhedron.[20–24]

In our first paper on molecular mechanics calculations of copper(II) chelates with *N,N*-dialkylated amino acids[25] we tried to reproduce the enantioselectivity effect in *bis*(*N,N*-dimethylvalinato)copper(II) as observed in chloroform solution (Table 1). Surprisingly, molecular mechanics calculations yielded a much higher (9.47 kJ mol^{-1}) enantioselectivity effect than was obtained experimentally. The result was attributed to bad parameterisation of the force field. Empirical parameters appeared to be too rigid, *i.e.*, they did not enable distortion of the coordination polyhedron.[25] Only when a "looser" force field was used, was the enantioselectivity effect correctly estimated, virtually at the limit of experimental error.[26] Quite analogous results were obtained for *bis*(*N,N*-dimethylisoleucinato)copper(II).[27]

The crystal structure of *bis*(*N,N*-dimethylvalinato)copper(II)[28] confirmed the results of molecular mechanics calculations. The conformer found in the crystal state (Fig. 3) corresponds to the most stable conformation (among 21 conformers) as obtained by molecular mechanics calculations. The conformer has a very close approach of bulky isopropyl groups which destabilize the MLL complex and leads to the distortion of the copper(II) coordination polyhedron. Unfortunately, the exact form of distorted coordination polyhedron was not obtained, a result too which led us to develop new models for interactions in the copper(II) coordination sphere.[20–24]

Conformational analysis of the MLD isomer of *bis*(*N,N*-diethylalaninato)-copper(II) correctly predicted the most stable conformer, found in the crystal state, among 190 possible conformations of the molecule.[29] Calculation on aqua*bis*(*L*-*N,N*-diethylalaninato)copper(II)[30] revealed that the most stable conformer did not correspond to the conformer obtained in the crystal structure. The calculated strain energy of the crystal conformation was about 4 kJ mol^{-1} higher than the energy of

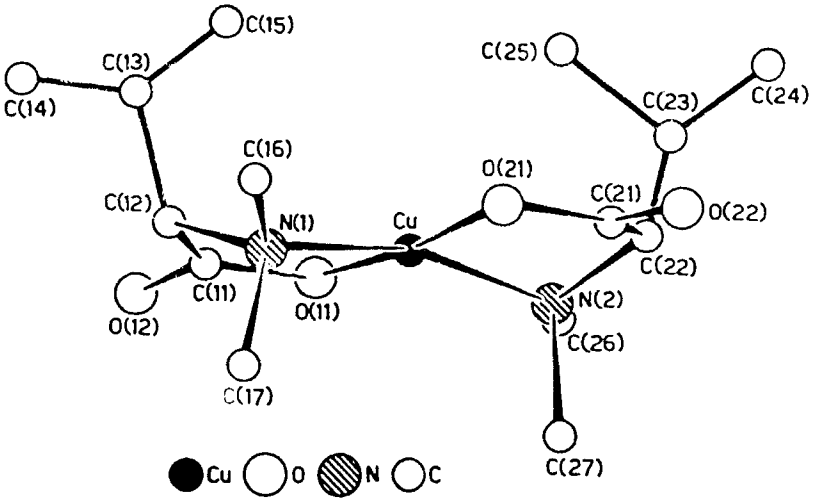


Figure 3 The structure of *bis*(*L*-*N,N*-dimethylvalinato)copper(II) as found in the crystal state. Taken from ref. 28.

the most stable conformer. This fact was tentatively attributed to the additional stabilization of the molecular conformation by intermolecular hydrogen bonds.

In spite of the existence of discrete C=O · · · H-OH hydrogen bridges, the conformation of aqua*bis*(*N*-*tert*-butyl-*N*-methylglycinato)copper(II) corresponds to the most stable conformer predicted theoretically.[31] Also, crystal conformation does not correspond to the conformer with the lowest strain energy of the red modification of *bis*(*N*-*tert*-butyl-*N*-benzylglycinato)copper(II); the crystal conformation is about 13 kJ mol^{-1} higher in energy than the most stable conformation.[32] This suggests the influence of intramolecular interactions in defining the molecular conformation (presumably the stacking of aromatic rings).

Calculations for aqua*bis*(*L*-*N*,*N*-dimethylthreoninato)copper(II) did not predict the conformation in the crystal state.[33] The calculated strain energy of the crystal conformation is about 21 kJ mol^{-1} higher than the energy of the most stable conformer. Obviously, conformation is determined not only with the intramolecular, but also with intermolecular interactions, mostly hydrogen bonding.

CONCLUSIONS

Considering results concerning the stereochemistry of copper(II) chelates with *N*-alkylated amino acids reported mostly by Russian authors and our group, the following conclusions can be drawn. Enantioselectivity effects in water solutions of copper(II) complexes with *N*-alkylated amino acids are closely connected with the binding of the water molecule to the apical position of the coordination polyhedron. There is no simple rule as to which complex form MLL (MDD) or MLD is more stable. Stability is influenced by the substituents on the coordinating nitrogen atom. In some cases, aromatic substituents (such as benzyl) can stabilize the complex presumably because of stacking effects. Finally, the stability of copper(II) chelates can be also influenced by ligand-ligand interactions involving the amino acid side chain.

References

1. R.D. Gillard, H.M. Irving, R.M. Parkins, N.C. Payne and L.D. Pettit, *J. Chem. Soc. A*, 1159 (1966).
2. Vl. Simeon and O.A. Weber, *Croat. Chem. Acta*, **38**, 161 (1966).
3. D.S. Barnes and L.D. Pettit, *J. Inorg. Nucl. Chem.*, **33**, 2177 (1971).
4. V.A. Davankov, S.V. Rogozhin and A.A. Kurganov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 204A (1971).
5. V.A. Davankov and A.V. Semechkin, *J. Chromatogr.* **141**, 313 (1977).
6. T.V. Timofeeva, A.A. Kurganov, V.A. Davankov and Yu. T. Struchkov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2484 (1987).
7. V. Noethig-Laslo and N. Paulić, *J. Chem. Soc., Dalton Trans.*, 2045 (1992).
8. R.E. Bowman and H.H. Stroud, *J. Chem. Soc.*, 1342 (1950).
9. P. Quitt, J. Hellerbach and K. Vogler, *Helv. Chim. Acta*, **46**, 327 (1963).
10. L.B. Kier and D. Dhawan, *J. Pharm. Sci.*, 1058 (1962).
11. C.P. Nash and W.P. Schaefer, *J. Am. Chem. Soc.*, **21**, 1319 (1964).
12. T. Yasui, *Bull. Chem. Soc. Jpn.*, **38**, 1746 (1965).
13. F. Basolo and Y.T. Chen. *J. Am. Chem. Soc.*, **76**, 953 (1954).
14. S.V. Rogozhin, V.A. Davankov, A.A. Kurganov and G.I. Timofeeva, *Zh. Neorg. Khim.*, **19**, 3294 (1974).

15. V.A. Davankov, S.V. Rogozhin, Yu. T. Struchkov, G.G. Aleksandrov and A.A. Kurganov, *J. Inorg. Nucl. Chem.*, **38**, 631 (1976).
16. S.R. Niketić and Kj. Rasmussen, *The Consistent Force Field: A Documentation, Lecture Notes in Chemistry 3*, (Springer, Berlin, 1977).
17. Kj. Rasmussen, *Potential Energy Functions in Conformational Analysis, Lecture Notes in Chemistry 37*, (Springer, Berlin 1985).
18. U. Burkert and N.L. Allinger, *Molecular Mechanics*, (American Chemical Society, Washington, D.C., 1982).
19. G.R. Brubaker and D.W. Johnson, *Coord. Chem. Rev.*, **53**, 1 (1984).
20. J. Sabolović, Kj. Rasmussen and N. Raos, *Croat. Chem. Acta*, **62**, 495 (1989).
21. J. Sabolović and N. Raos, *Polyhedron*, **9**, 1277 (1990).
22. J. Sabolović and N. Raos, *Polyhedron*, **9**, 2419 (1990).
23. J. Sabolović, N. Raos and Kj. Rasmussen, *Polyhedron*, **10**, 2079 (1991).
24. J. Sabolović, Polyhedron, **12**, 1107 (1993).
25. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **56**, 79 (1983).
26. N. Raos and Vl. Simeon, *Croat. Chem. Acta*, **58**, 127 (1985).
27. N. Raos and Vl. Simeon, *Croat. Chem. Acta* **57**, 1217 (1984).
28. B. Kaitner, B. Kamenar, N. Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **15**, 373 (1987).
29. B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 105 (1992).
30. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **25**, 337 (1992).
31. B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **26**, 95 (1992).
32. B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, **29**, 297 (1993).
33. B. Kaitner, G. Ferguson, N. Paulić and N. Raos, *J. Coord. Chem.*, in press.
34. V.A. Davankov, S.V. Rogozhin, A.A. Kurganov and L. Ya. Zhuchkova, *J. Inorg. Nucl. Chem.*, **37**, 369 (1975).
35. A.A. Kurganov, L. Ya. Zhuchkova and V.A. Davankov, *Koord. Khim.*, **4**, 1503 (1978).
36. T.S. Cameron, K. Prout, F.J.C. Rosotti and D. Steele, *J. Chem., Soc., Dalton Trans.*, 2626 (1973).
37. G.G. Aleksandrov, Yu. T. Struchkov, A.A. Kurganov, S.V. Rogozhin and V.A. Davankov, *Zh. Strukt. Khim.*, **13**, 671 (1972).
38. G.G. Aleksandrov, Yu. T. Struchkov and A.A. Kurganov, *Zh. Strukt. Khim.*, **14**, 492 (1973).
39. B. Kamenar, M. Penavić, A. Škorić, N. Paulić, N. Raos and Vl. Simeon, *J. Coord. Chem.*, **17**, 85 (1988).
40. B. Kaitner, N. Paulić and N. Raos, *J. Coord. Chem.*, **22**, 269 (1991).
41. G.G. Aleksandrov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **16**, 228 (1975).