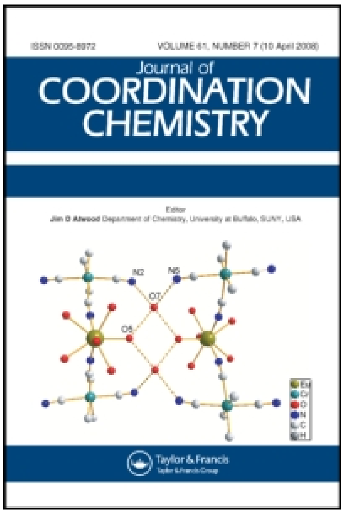

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REACTION OF BIS(β-ALANINATO)COPPER(II) WITH FORMALDEHYDE: X-RAY CRYSTAL STRUCTURE OF AQUABIS(*N,N*-DIMETHYL-β-ALANINATO)COPPER(II) HEXAHYDRATE

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REACTION OF BIS(β-ALANINATO)COPPER(II) WITH FORMALDEHYDE: X-RAY CRYSTAL STRUCTURE OF AQUABIS(*N*,*N*-DIMETHYL-β-ALANINATO)COPPER(II) HEXAHYDRATE

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The reaction of bis(β-alaninato)copper(II) with formaldehyde results in the formation of blue crystals of aquabis(*N*,*N*-dimethyl-β-alaninato)copper(II) hexahydrate, $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$ which crystallize in the monoclinic space group $C2/c$ with unit cell dimensions $a = 20.799(2)$, $b = 8.112(1)$, $c = 23.639(1)$Å, $\beta = 96.50(1)°$ and $Z = 8$. The structure has been refined to final $R = 0.047$ and $R_W = 0.053$ for 1690 reflections with $I \geqslant 2.55\sigma(I)$.

KEY WORDS: Copper(II), alanine, formaldehyde, methylation, X-ray structure

INTRODUCTION

Extensive studies have been caarried out on the reactions of formaldehyde with α-aminoacidato metal(II) complexes.[1–9] By contrast, there has only been one reported instance of such reactions involving β-aminoacidato metal(II) complexes, namely, where bis(β-alaninato)copper(II) reacts with formaldehyde and ammonia resulting in the formation of [3*N*,7*N*-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)-di-3-propionato]copper (II).[10]

In the present study, we report the reaction of bis(β-alaninato)copper(II) with formaldehyde in the absence of base which leads to the formation of aquabis(*N*,*N*-dimethyl-β-alaninato)copper(II) hexahydrate. A full X-ray structural analysis of the compound has been performed and the results are presented herewith.

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EXPERIMENTAL

Reagents

β-Alanine was supplied by the B.D.H. Chemical Company while formaldehyde was obtained as a 37% w/v aqueous solution from May and Baker.

Bis(β-alaninato)copper(II) tetrahydrate [Cu(β-ala)$_2$.4H$_2$O] was prepared according to the method of Mitsui *et al.*[11]

*Preparation of aquabis(*N,N*-dimethyl-β-alaninato)copper(II) hexahydrate*

A mixture consisting of 10 cm^3 of a 37% w/v solution of formaldehyde (0.12 mol) and Cu(β-ala)$_2$.4H$_2$O (2.0 g, 0.006 mol) was stirred thoroughly. The resultant blue solution (pH 5.3) was allowed to evaporate in air at room temperature. After 5 weeks, blue, plate-like crystals were formed. These were filtered and washed with ethanol-acetone mixture and were finally dried in the oven at 50°C overnight. Yield 0.2 g (8%). *Anal.*: Calcd. for $C_{10}H_{34}N_2O_{11}Cu$: C, 28.47; H, 4.78; N, 6.64%. Found: C, 28.52; H, 4.93; N, 6.62%.

Determination of crystal structure of $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$

Intensity data for a blue, plate-like crystal of $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$ (0.06 × 0.60 × 0.68 mm) was measured at room temperature (293K) on an Enraf-Nonius CAD4*F* diffractometer using MoK_α radiation (graphite monochromator), $\lambda = 0.7107$Å. The ω: 2θ scan technique was employed to measure 2977 reflections up to a maximum Bragg angle of 22.5°. The data set was corrected for Lorentz and polarization effects and an analytical absorption correction was also applied[12] such that the maximum and minimum transmission factors were 0.931 and 0.375, respectively. Crystal data are summarized in Table 1.

Table 1 Crystal data for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$.

Formula	$C_{10}H_{34}CuN_2O_{11}$
Formula weight	421.9
Crystal system	monoclinic
Space group	$C2/c$, (C_{2h}^6, No 15)
a(Å)	20.799(2)
b(Å)	8.112(1)
c(Å)	23.639(1)
β(deg)	96.50(1)
V(Å^3)	3962.8
Z	8
D_{calcd}, g cm^{-3}	1.414
F(000)	1800
μ, mm^{-1}	1.122
Data collected	2977
Unique data	2589
Data with $I \geqslant 2.5\sigma(I)$	1690
R	0.047
g	0.0107
R_W	0.053
ρ_{max}, (e Å^{-3})	0.56

Table 2 Fractional atomic coordinates ($\times 10^5$ for Cu, $\times 10^4$ for remaining atoms) for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$.

Atom	x/a	y/b	x/c
Cu	24824(2)	−776(6)	12402(2)
O(1)	2816(2)	9(4)	2040(1)
O(2)	2946(2)	−626(5)	2941(2)
O(3)	2155(2)	−560(5)	455(1)
O(4)	2045(2)	307(4)	−432(1)
O(w1)	2455(1)	2660(4)	1177(1)
N(1)	1542(2)	−316(4)	1419(2)
N(2)	3429(2)	−459(5)	1082(2)
C(1)	2594(2)	−465(6)	2484(2)
C(2)	1881(2)	−838(7)	2463(2)
C(3)	1459(2)	112(6)	2021(2)
C(4)	1330(3)	−2036(6)	1284(2)
C(5)	1101(2)	796(7)	1053(2)
C(6)	2394(2)	6(4)	22(2)
C(7)	3108(2)	301(7)	62(2)
C(8)	3490(3)	−815(7)	469(2)
C(9)	3680(3)	−1963(7)	1398(2)
C(10)	3844(2)	940(7)	1294(2)
O(w2)	−51(1)	2348(5)	−19(1)
O(w3)	710(2)	−146(4)	4442(2)
O(w4)	719(2)	4577(4)	1947(2)
O(w5)	448(2)	4840(4)	747(2)
O(w6)	5451(2)	4623(5)	3243(2)
O(w7)	5000	7254(6)	2500
O(w8)	5000	8046(6)	7500

The structure was solved by the Patterson method and refined by full-matrix least-squares procedures.[12] Non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions except for those on the H_2O molecules which were not located. A weighting scheme of the form $w = [\sigma^2(F) + |g|F^2]^{-1}$ was introduced and the refinement continued until covergence; final refinement details are listed in Table 1. The analysis of variance showed no special features indicating that an appropriate weighting scheme had been employed. Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Figure 1 which was drawn using ORTEP[13] with 25% probability ellipsoids. Selected interatomic bond distances and angles are listed in Table 3. Scattering factors for neutral Cu (corrected for f' and f'') were from ref. 14, while those for the remaining atoms were those incorportated in SHELX-76.[12]

RESULTS AND DISCUSSION

The crystal structure of the reaction product $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$ established the *N*,*N*-dimethylation of the Cu(β-ala)$_2$ by formaldehyde. The two β-alanine residues in the product are *trans* with respect to each other which means that the initial *trans* Cu(β-ala)$_2$.$4H_2O$[11] has retained its ligand configuration. Such retention of the *trans* ligand configuration is usual as reactions of amino acid complexes

Table 3 Selected bond distances (Å) and angles (°) for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$.

Cu-O(1)	1.941(3)	Cu-O(3)	1.943(3)
Cu-N(1)	2.057(4)	Cu-N(2)	2.068(4)
Cu-O(w1)	2.226(3)	O(1)-C(1)	1.254(6)
O(2)-C(1)	1.242(6)	O(3)-C(6)	1.274(6)
O(4)-C(6)	1.249(6)	N(1)-C(3)	1.494(6)
N(1)-C(4)	1.487(6)	N(1)-C(5)	1.492(6)
N(2)-C(8)	1.498(6)	N(2)-C(9)	1.494(6)
N(2)-C(10)	1.478(6)		

O(1)-Cu-O(3)	170.5(1)	O(1)-Cu-N(1)	92.7(2)
O(1)-Cu-N(2)	86.5(2)	O(1)-Cu-O(w1)	91.9(1)
O(3)-Cu-N(1)	86.5(1)	O(3)-Cu-N(2)	92.0(1)
O(3)-Cu-O(w1)	97.6(1)	N(1)-Cu-N(2)	165.9(2)
N(1)-Cu-O(w1)	95.2(1)	N(2)-Cu-O(w1)	98.9(1)
Cu-O(1)-C(1)	132.8(3)	O(1)-C(1)-O(2)	121.5(4)
O(1)-C(1)-C(2)	119.2(4)	O(2)-C(1)-C(2)	119.2(4)
Cu-O(3)-C(6)	124.7(3)	O(3)-C(6)-O(4)	121.3(4)
O(3)-C(6)-C(7)	118.8(4)	O(4)-C(6)-C(7)	119.9(5)
Cu-N(1)-C(3)	112.9(3)	Cu-N(1)-C(4)	108.0(3)
Cu-N(1)-C(5)	111.1(3)	C(3)-N(1)-C(4)	111.1(1)
C(3)-N(1)-C(5)	106.6(4)	C(4)-N(1)-C(5)	107.2(4)
Cu-N(2)-C(8)	113.0(3)	Cu-N(2)-C(9)	108.6(3)
Cu-N(2)-C(10)	110.8(2)	C(8)-N(2)-C(9)	105.2(4)
Cu-N(2)-C(10)	111.4(4)	C(9)-N(2)-C(10)	107.5(4)

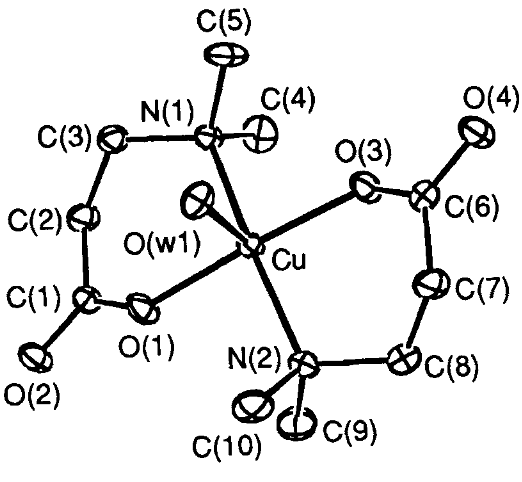

Figure 1 Molecular structure and crystallographic numbering scheme for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$.

with aldehydes have always resulted in the *trans* metal-containing product regardless of whether the starting ligands are *cis* or *trans*.[1-7]

In the complex, the copper atom is five-coordinate and exists in a distorted square pyramidal geometry with an N_2O_2 donor set of two β-alanine ligands defining the basal plane and a coordinated water molecule in the axial position (Fig. 1). The O(1),

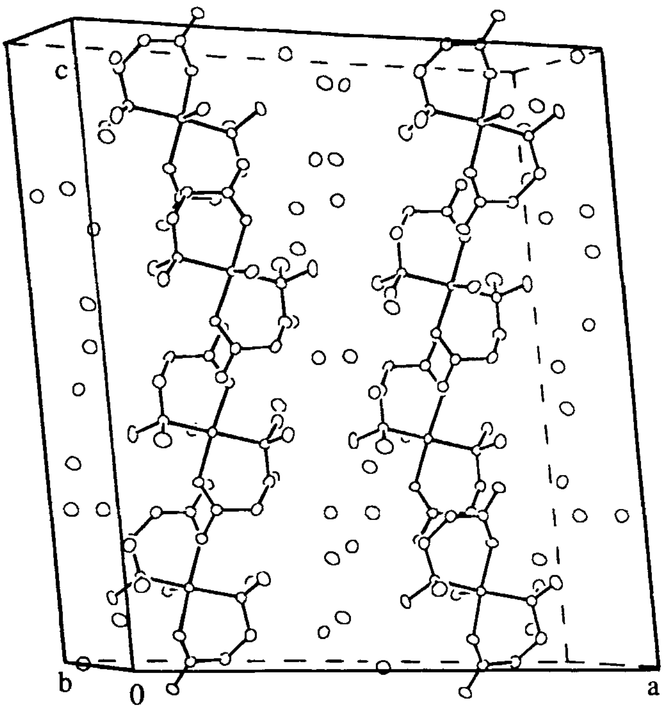

Figure 2 Unit cell contents for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$.

O(3). N(1) and N(2) atoms have deviations of 0.040(3), 0.038(4), −0.049(4) and −0.054(4)Å, respectively, from the least-squares plane through these atoms and the copper atom lies 0.207(5)Å out of this plane in the direction of the coordinated water molecule. Characteristically for Cu(II), the bond to the apical water is longer than those to the donor atoms in the coordination square[15,16] but the Cu-O(w1) bond distance of 2.226(3)Å is shorter than that found in similar compounds.[1,7,15-18] There is shortening of the Cu-O bond lengths and lengthening of the Cu-N bond lengths of the coordination square compared to those of the corresponding bond lengths of Cu(β-ala)$_2$.4H$_2$O.[11] Although this is similarly observed for [3*N*,7*N*-(1,3,5,7-tetraazabicyclo[3.3.1]-nonyl)-di-3-propionato]copper(II),[10] the present complex shows a shortening and lengthening factor of about 2 compared to the former.

As can be seen from the molecular formula, there are a total of six water molecules of crystallization in the lattice per complex molecule. Two of these (*i.e.*, the O(w7) and O(w8) atoms) lie on a crystallographic 2-fold axis and hence there are seven independent water molecules in the lattice. A packing diagram for $[Cu(C_5H_{10}NO_2)_2(OH_2)].6H_2O$ is shown in Fig. 2 from which it can be seen that the lattice is comprised of layers of complex molecules sandwiched between layers of water molecules. As expected from the molecular formula, there is a complex H-bonding in the lattice and the most significant contacts are listed in table S(4) of the supplementary materia.* There are, however, relatively few contacts involving

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*Supplementary data, including H atom positions, anisotropic thermal parameters, full lists of bond lengths and angles, and observed and calculaated structure factors are available from the authors on request.

the complex. The coordinated water molecule forms two close contacts with the O(2) and O(4) atoms (*i.e.*, the non-coordinating carboxylate O atoms) of symmetry related complex molecules at 2.707 and 2.716Å, respectively. Other interactions involving the complex occur between the O(4) and O(w3) atoms at 2.763Å and between O(2) and O(w4) at 2.766Å.

Recent studies on the non-basic reactions of α-amino acid chelates with formaldehyde have resulted in observations of oxazolidine or *N*-substituted metaformaldehyde metal(II) complexes.[5,6,9,19] The present reaction of bis(*β*-alaninato)copper(II) with formaldehyde in the absence of base has resulted in the *N*,*N*-dimethylation of the former. To our knowledge, this is the first instance of the methylation of an amino acid chelate by formaldehyde alone. Methylation of amines involving the Eschweiler-Clark reaction[20–25] requires the addition of substantial amount of formic or acetic acid as the reducing agent or hydrogen donor. Other similar reductive methylations involves initial hydroxymethylation by formaldehyde, followed by catalytic reduction[25] or other reducing agents such as tetracarboxylhydridoferrate and borohydride[25–28] under acidic conditions.

The present *N*,*N*-dimethylation of bis(*β*-alaninato)copper(II) may be considered to proceed *via* a mechanism similar to that proposed by Manninen[22] whereby initial hydroxymethylated species formed give rise to the copper(II) carbonium-immonium ion which is then reduced to (*N*-methyl-*β*-alaninato)copper(II). The process is repeated to yield the final *N*,*N*-dimethyl product.

The Eschweiler-Clark methylation procedure uses excess formic acid (compared to the formaldehyde used here). In the present synthesis of (*N*,*N*-dimethyl-*β*-alaninato)copper(II) the formic acid present in the formaldehyde used and the formic acid formed from the oxidation of formaldehyde is sufficient to effect the reduction of *N*-hydroxymethyl substituent to the *N*-methyl derivative. However, the low temperature (room temperature) and lower formic acid concentration employed here results in a slower reaction (about 1 month) and a rather low yield.

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