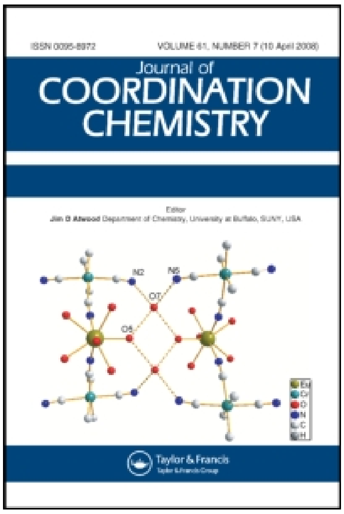

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A NOVEL AQUA[3*N*,5*N*-METHYLAMINO(1,3,5-OXADIAZACYCLOHEXYL)DIACETATO]COPPER(II) MONOHYDRATE FORMED BY THE CONDENSATION OF BIS(GLYCINATO)COPPER(II) WITH FORMALDEHYDE AND AMMONIA

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A NOVEL AQUA[3*N*,5*N*-METHYLAMINO(1,3,5-OXADIAZACYCLOHEXYL)DIACETATO]COPPER(II) MONOHYDRATE FORMED BY THE CONDENSATION OF BIS(GLYCINATO)COPPER(II) WITH FORMALDEHYDE AND AMMONIA

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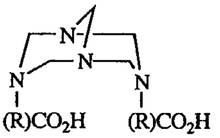
The Mannich reaction involving *bis*(glycinato)copper(II), formaldehye and ammonia over the pH range 6.0–6.5 results in the formation of the title compound, aqua[3*N*,5*N*-methylamino(1,3,5-oxadiazacyclohexyl)diacetato]copper(II) monohydrate (2), in which one of the amino nitrogen atoms of *bis*(glycinato)copper(II) is fully substituted while the other experiences only partial substitution. The crystal structure of **2** shows the copper atom to have square pyramidal geometry with a N_2O_2 basal plane and a water molecule in the apical site. Crystals of **2** are monoclinic, space group $P2_1/c$ with unit cell dimensions a = 11.756(2), b = 7.903(1), c = 12.583(1) Å, β = 95.27(1)°, V = 1164.0(3) Å^3, Z = 4. The structure was refined by a full-matrix least-squares procedures to R = 0.037 for 2253 observed reflections.

KEYWORDS: glycine, formaldehyde, ammonia, copper(II), crystal structure

INTRODUCTION

Recent studies have shown that copper(II), nickel(II), zinc(II) and cobalt(II) chelates of glycine, α-alanine and β-alanine react with formaldehyde and ammonia at pH ~ 8.5 to give the respective metal(II) complexes of **1**.[1–5]



R = CH_2, CH_3CH, CH_2CH_2

1

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*Authors for correspondence.

In this contribution, the Mannich reaction of *bis*(glycinato)copper(II) with formaldehyde and ammonia over the pH range 6.0–6.5 which leads to the formation of aqua[3*N*,5*N*-methylamino(1,3,5-oxadiazacyclohexyl)diacetato]copper(II) monohydrate (**2**) is reported. The crystal structure determination of **2** has been performed and the results of this study are discussed herein.

EXPERIMENTAL

Reagents

Glycine was obtained from the BDH Chemical Company and formaldehyde was supplied by May and Baker as a 37% w/v aqueous solution. *Cis-bis*(glycinato) copper(II) monohydrate, *cis*-$Cu(gly)_2 \cdot H_2O$, was prepared as reported previously.[6]

Preparation of 1

A reactioin mixture consisting of an aqueous solution of *cis*-$Cu(gly)_2 \cdot H_2O$ (1 g, 0.004 mol) and 10 cm^3 of a 37% w/v solution of formaldehyde (0.12 mol) was stirred thoroughly and its pH adjusted to 6.0 by the slow addition of concentrated ammonia solution. On standing for 8 days, deep blue crystals appeared. These were filtered, washed with ethanol and finally dried *in vacuo* for 5 h. Yield 0.4 g (30%). Analysis, found: C, 28.99; H, 5.16; N, 12.68%. Calcd. for $C_8H_{15}N_3O_6Cu$. H_2O: C, 29.05; H, 5.18; N, 12.70%.

Crystallography

Intensity data for a crystal (0.10×0.39×0.48 mm) were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized MoKα radiation, $\lambda = 0.71073$ Å, employing the $\omega - 2\theta$ scan technique such that θ_{max} was 27.5°. The data set was corrected for Lorentz and polarization effects[7] and for absorption (range of transmission factors: 0.864–1.511).[8] Of the 3130 reflections measured, 2991 were unique and of these 2253 satisfied the $I \geq 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

Crystal data for **2**: $C_8H_{17}CuN_3O_7$, $M = 330.8$, monoclinic, space group $P2_1/c$, $a = 11.756(2)$, $b = 7.903(1)$, $c = 12.583(1)$ Å, $\beta = 95.27(1)°$, $V = 1164.0(3)$ Å^3, $Z = 4$, $D_{calc} = 1.887$ g cm^{-3}, $F(000) = 684$, $\mu = 19.14$ cm^{-1}.

The structure was solved by direct methods[9] and refined by a full-matrix least-squares procedure based on F.[7] Non-H atoms were refined with anisotropic thermal parameters and H atoms were refined isotropically; O-bound H atoms were not located in the study. At convergence, $R = 0.037$ and $R_w = 0.054$ (sigma weights). The analysis of variance showed no special features and the maximum electron density peak in the final difference map was 0.61 e Å^{-3}. Fractional atomic coordinates are listed in Table 1, selected interatomic parameters are given in Table 2 and the numbering scheme employed is shown in Figure 1 which was drawn with the ORTEP program at 30% probability ellipsoids.[10] Listings of thermal

Table 1 Fractional atomic coordinates for **2**.

Atom	*x/a*	*y/b*	*z/c*
Cu	0.77878(5)	0.19450(7)	0.16821(4)
O(1)	0.7263(3)	0.4215(4)	0.1371(2)
O(1w)	0.6032(3)	0.0751(5)	0.0981(3)
O(2w)	0.4066(3)	0.2576(5)	0.5103(3)
O(2)	0.5920(3)	0.5955(4)	0.1787(3)
O(3)	0.9460(2)	0.0699(4)	0.3607(2)
O(4)	0.8420(3)	0.1671(4)	0.0353(2)
O(5)	0.8737(3)	-0.0323(4)	-0.0791(2)
N(1)	0.7253(3)	0.2373(5)	0.3086(3)
N(2)	0.7634(3)	-0.0543(5)	0.3686(3)
N(3)	0.8487(3)	0.0314(4)	0.2026(2)
C(1)	0.6512(4)	0.4717(5)	0.1964(3)
C(2)	0.6362(4)	0.3664(6)	0.2931(4)
C(3)	0.6867(4)	0.0877(6)	0.3661(4)
C(4)	0.8742(4)	-0.0272(6)	0.4235(3)
C(5)	0.9597(4)	-0.0129(6)	0.2655(3)
C(6)	0.7733(4)	-0.1319(6)	0.2672(3)
C(7)	0.8616(5)	-0.1125(6)	0.0994(4)
C(8)	0.8601(4)	0.0162(6)	0.0109(3)

Table 2 Selected bond distances (Å) and angles (°) for **2**.

Cu-O(1)	1.926(3)	Cu-O(4)	1.904(3)
Cu-O(1w)	2.366(3)	Cu-N(1)	1.959(3)
Cu-N(3)	1.996(3)	O(1)-C(1)	1.270(5)
O(2)-C(1)	1.209(5)	O(3)-C(4)	1.431(5)
O(3)-C(5)	1.388(5)	O(4)-C(8)	1.254(5)
O(5)-C(8)	1.220(5)	N(1)-C(2)	1.462(6)
N(1)-C(3)	1.478(6)	N(2)-C(3)	1.439(6)
N(2)-C(4)	1.433(6)	N(2)-C(6)	1.431(5)
N(3)-C(5)	1.470(5)	N(3)-C(6)	1.487(5)
N(3)-C(7)	1.468(5)	C(1)-C(2)	1.498(6)
C(7)-C(8)	1.507(6)		
O(1)-Cu-O(4)	94.1(1)	O(1)-Cu-O(1w)	92.5(1)
O(1)-Cu-N(1)	84.2(1)	O(1)-Cu-N(3)	174.4(1)
O(4)-Cu-O(1w)	91.4(1)	O(4)-Cu-N(1)	174.7(2)
O(4)-Cu-N(3)	84.4(1)	O(1w)-Cu-N(1)	93.7(1)
O(1w)-Cu-N(3)	93.0(1)	N(1)-Cu-N(3)	96.8(1)
Cu-O(1)-C(1)	113.5(3)	Cu-O(4)-C(8)	114.3(3)
Cu-N(1)-C(2)	106.6(3)	Cu-N(1)-C(3)	116.2(3)
Cu-N(3)-C(5)	110.8(3)	Cu-N(3)-C(6)	110.0(3)
Cu-N(3)-C(7)	105.8(3)		

parameters, H atom parameters, all bond distances and angles, and structure factor amplitudes are available on request from ERTT.

RESULTS AND DISCUSSION

The molecular structure of the reaction product, **2**, is shown in Figure 1 and selected interatomic parameters are collected in Table 2. The structure determination

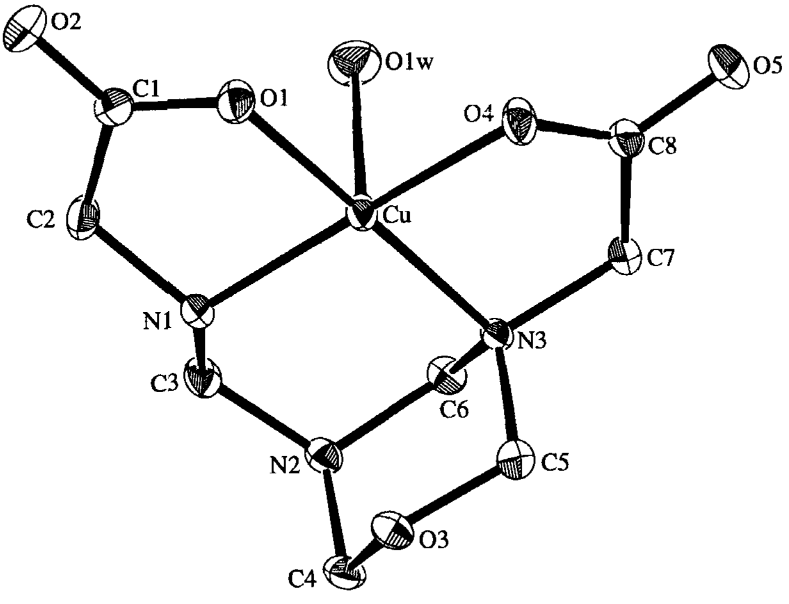

Figure 1 Molecular structure and crystallographic numbering scheme for **2**.

establishes that the condensation of *cis*-Cu(gly)$_2$·H$_2$O with formaldehyde and ammonia results in the bridging of the two amino nitrogen atoms of the chelated glycine moieties, *i.e.*, at N(1) and N(3), by a dimethyleneamine group. Further, a dimethyleneether group links the amine N(2) and N(3) atoms leading to the formation of a six-membered C_3N_2O ring. Such a linkage, which is without precedence in the reactions of chelated amino acids with aldehyde, could be attributed to the difference in reactivities of the amino nitrogen atoms of *cis*-Cu(gly)$_2$·H$_2$O. An indication that the two amine nitrogen atoms are different is given in the crystal structure of *cis*-Cu(gly)$_2$·H$_2$O,[6] in which the nitrogen atom of one of the two glycine residues forms two hydrogen bonds whereas the other only forms one hydrogen bond. It is also noteworthy that the two glycine residues in **2**, retains the initial *cis*-configuration of the ligands as found in *cis*-Cu(gly)$_2$·H$_2$O.[6]

A related investigation[11] has shown that in the condensation of the coordinated mixed amino acid *L*-alaninato-*L*-glycinato, whilst coordinated to a copper(II) centre, with formaldehyde and ammonia, the two amino acid residues are joined by an identical linkage to that observed in **2**. In this instance, the chelated glycine (which exhibits a much faster proton exchange rate than the chelated alanine) is disubstituted while the alanine residue is mono-substituted.

In the complex **2**, the copper atom is five-coordinate and exists in a distorted square pyramidal geometry. In this description, the basal plane is defined by two oxygen atoms, derived from two monodentate carboxylate groups, and two nitrogen atoms, derived from the glycine portions of the polydentate ligand. The apical position is occupied by a water molecule. The major distortion from the ideal geometry is manifested in the N(1)-Cu-N(3) chelate angle of 96.8(1)°. The mean deviation of the atoms defining the basal plane is 0.004 Å and copper atom lies

0.0901(5) Å out of this plane in the direction of O(1w) atom. The Cu-ligand bond distances are as found in related systems.[2,6,12] Characteristically, the Cu-O(apical) bond distance is longer than the Cu-O bonds in the basal plane[12–14] but the separation of 2.366(3) Å is shorter than is found in octahedral copper(II) complexes.[6,15,16]

The two five-membered rings involving the glycine residues are puckered, as emphasized by the values of the Cu/N(1)/C(2)/C(1) and Cu/N(3)/C(7)/C(8) torsion angles of $-24.9(5)$ and $20.5(4)°$, respectively. The two Cu-N(1)-C(3)-N(2)-C(6)-N(3) and N(2)-C(4)-O(3)-C(5)-N(3)-C(6) six-membered rings each adopt a chair conformation. As expected, there a number of significant hydrogen-bonding contacts in the lattice; a detailed analysis is hampered somewhat as the oxygen-bound hydrogen atoms were not located in the structure determination. The copper-bound water molecule forms two contacts, each with symmetry related lattice water molecules, *i.e.*,O(1w)...O(2w)^{I} is 2.800(5) Å (symmetry operation: x, $0.5 - y$, $-0.5 + z$) and O(1w)...O(2w)^{II} is 2.853(5) Å ($1 - x$, $-0.5 + y$, $0.5 - z$). The lattice water molecule forms two additional contacts, one with the O(2)^{II} carbonyl atom at 2.703(5) Å and the other with the N(2)^{III} atom at 3.075(5)Å ($1 - x$, $-y$, $1 - z$). The N(1)-H atom forms two contacts with the O(4)CO(5)^{IV} carboxylate group (x, $0.5 - y$, $-0.5 + z$) such that N(1)-H...O(4) is 2.48(4) Å and N(1)-H...O(5) is 2.47(4) Å.

When the present reaction is carried out at pH 7.0–9.0, the copper(II) complex of **1** (R = CH_2) has been isolated (70% yield).[17] Thus, these results suggest that **2** could be a possible intermediate in the formation of the former complex.

Acknowledgements

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