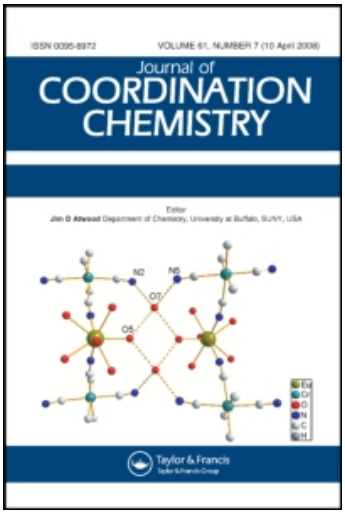

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MANNICH REACTION OF *BIS*(GLYCINATO)COPPER(II), FORMALDEHYDE AND ACETAMIDE: X-RAY CRYSTAL STRUCTURE OF BIS[(*N,N*-DI-*N'*-METHYLACETAMIDO)GLYCINATO]COPPER(II) DIHYDRATE

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MANNICH REACTION OF *BIS*(GLYCINATO)-COPPER(II), FORMALDEHYDE AND ACETAMIDE: X-RAY CRYSTAL STRUCTURE OF BIS[(*N*,*N*-DI-*N'*-METHYLACETAMIDO)-GLYCINATO]COPPER(II) DIHYDRATE

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The Mannich reaction of bis(glycinato)copper(II) with formaldehyde and acetamide results in the formation of bis[(N,N-di-N'-methylacetamido)glycinato]copper(II) dihydrate, $C_{16}H_{28}N_6O_8Cu.2H_2O$, which crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions a = 11.300(2), b = 13.041(2), c = 8.799(1)Å, β = 99.51(1)° and Z = 2. The structure has been refined to final R = 0.034 and R_w = 0.049 for 2508 reflections with $F > 4.0\sigma(F)$.

KEYWORDS: bis(glycinato) copper (II), formaldehyde, acetaimde, X-ray structure

INTRODUCTION

Condensation reactions of the Mannich type involving amino acid chelates and formaldehyde have received considerable attention in recent years.[1,2] In this paper we report the reaction of *cis-bis*(glycinato)copper (II) with formaldehyde and acetamide which leads to the formation of *bis*[(*N*,*N*-di-*N'*-methylacetaimdo)glycinato]-copper(II) dihydrate, confirming the finding of an earlier investigation.[2] A full X-ray structural analysis of the copper(II) complex has been performed and the results are discussed herein.

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EXPERIMENTAL

Reagents

Glycine and acetamide were obtained from B.D.H. 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 described previously.[3]

Preparation of bis[N,N-di-N'-methylacetaimdo)glycinato]copper(II) dihydrate, $C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$

A reaction mixture consisting of *cis*-Cu(gly)$_2 \cdot H_2O$ (1.0 g, 0.004 mol), acetamide (1.2 g, 0.02 mol) and formaldehyde (10 cm^3, 0.13 mol) was stirred thoroughly and then filtered. The pH of the filtrate was adjusted to 6.0 by the addition of concentrated ammonia solution. On standing for a week, the reaction mixture yielded blue crystals which were filtered, washed with a water-ethanol mixture and finally dried *in vacuo* for 4 h. Yield, 1.7 g (80%). *Anal.*: Calcd. for $C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$: C, 36.10; H, 6.06; N, 15.80%. Found: C, 36.64; H, 5.80; N, 15.63%.

Determination of crystal structure of $C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$

Diffraction data for a crystal with dimensions 0.78 × 0.28 × 0.82 mm were collected at 22°C with a Siemens P4 diffractometer using Mo-K_α radiation, λ = 0.71073Å. the θ–2θ scan was employed to measure a total of 3776 reflections such that $\theta_{max} < 30°$. Raw intensities collected were processed for Lorentz and polarization effects and for absorption; max. and min. transmission factors were 0.909 and 0.664, respectively. There were 2927 unique reflections of which 2508 satisfied the $F > 4.0\ \sigma(F)$ criterion of observability and these were used in the subsequent analysis. Crystal data and details of data collection are listed in Table 1.

Table 1 Crystal data and refinement details for $C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$.

Formula	$C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$
Formula weight	568.0
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	11.300(2)
b (Å)	13.041(2)
c (Å)	8.799(1)
β (°)	99.51(1)
Volume (Å)	1278.8(3)
Z	2
ρ_c (g cm^{-3})	1.475
F (000)	598
μ (cm^{-1})	9.22
Data collected	3776
Unique data	2927
Data with $F > 4.0\ \sigma(F)$	2508
R	0.034
R_w	0.049

The structure was solved using direct methods[4] with Siemens SHELXTL PC.[5] The structure was refined by the full-matrix least-squares method using 160 parameters. In the refinement, all non-hydrogen atoms were assigned anisotropic thermal parameters while the hydrogen atoms were refined using the riding model with fixed isotropic thermal parameters. A weighting scheme of the form $\omega = [\sigma^2(F) + gF^2]^{-1}$ was used and the refinement continued to final $R = 0.034$, $R_w = 0.049$ for $g = 0.0005$. Atomic coordinates for non-hydrogen atoms are listed in Table 2, bond lengths and angles in Table 3. The atom numbering scheme employed is shown in Figure 1, which was drawn with *ORTER*.[6]

RESULTS AND DISCUSSION

The molecular structure of the reaction product (Figure 1) establishes that *cis*-$Cu(gly)_2 \cdot H_2O$ has undergone a Mannich type reaction with formaldehyde and acetamide. Each chelated glycine has reacted with two molecules of acetamide to yield two *N*-methylacetamido groups, one which is free while the other coordinates to the central copper atom *via* its carbonyl oxygen. The two chelated glycine ligands in the reaction product are *trans* with respect to each other, a fact which implies that the initial *cis*-$Cu(gly)_2 \cdot H_2O$ complex has undergone rearrangement to give the observed *trans* ligand configuration in the final product.[3]

In the complex, the copper atom is hexa-coordinate and exists in a distorted octahedral environment. Two oxygen atoms and two nitrogen atoms derived from the glycine residues are coplanar with the copper atom, which is at a centre of symmetry. This set of CuN_2O_2 atoms forms the equatorial plane while the two carbonyl oxygen atoms [O(4)-Cu(1)-O(4a); symmetry operation a: $-x, -y, -z$, one from each of the two *N*-methylacetamido groups, occupy the axial positions in the coordination polyhedron. The methylacetamido carbonyl O(4) is at a distance of 2.496Å from the copper atom while the carboxylate O(1) is 1.938(1) Å from the

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x/a	*y/b*	*z/c*	U_{eq} #
Cu(1)	0	0	0	33(1)
O(1)	796(1)	747(1)	1783(1)	39(1)
O(2)	598(1)	1227(1)	4130(1)	43(1)
O(3)	-3945(1)	1088(1)	1605(2)	75(1)
O(4)	1221(1)	-1517(1)	1031(2)	52(1)
N(1)	-1240(1)	-371(1)	1361(2)	32(1)
C(1)	208(1)	823(1)	2884(2)	32(1)
C(2)	-1074(2)	419(1)	2603(2)	35(1)
C(3)	-2477(2)	-358(2)	470(2)	42(1)
N(2)	-3405(1)	-555(1)	1378(2)	47(1)
C(4)	-4086(2)	187(2)	1854(2)	51(1)
C(5)	-5039(2)	-193(2)	2726(3)	71(1)
C(6)	-965(2)	-1419(1)	2004(2)	38(1)
N(3)	168(1)	-1489(1)	2988(2)	38(1)
C(7)	1205(2)	-1560(1)	2428(2)	41(1)
C(8)	2317(2)	-1662(2)	3603(2)	60(1)
O(1w)	-5902(2)	2350(2)	2161(2)	81(1)
O(2w)	3042(2)	1680(2)	4575(2)	90(1)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses for non-hydrogen atoms.

Cu(1)-O(1)	1.938(1)	Cu(1)-N(1)	2.046(2)
Cu(1)-O(4)	2.496(1)	O(2)-C(1)	1.231(2)
O(1)-C(1)	1.265(2)	O(4)-C(7)	1.234(2)
O(3)-C(4)	1.210(3)	N(1)-C(3)	1.485(2)
N(1)-C(2)	1.491(2)	C(1)-C(2)	1.523(2)
N(1)-C(6)	1.493(2)	N(2)-C(4)	1.345(3)
C(3)-N(2)	1.442(3)	C(6)-N(3)	1.425(2)
C(4)-C(5)	1.506(3)	C(7)-C(8)	1.495(2)
N(3)-C(7)	1.348(2)		
O(1)-Cu(1)-N(1)	85.2(1)	O(1)-Cu(1)-(1a)	180.0(1)
N(1)-Cu(1)-0(1a)	94.8(1)	O(1)-Cu(1)-N(1a)	94.8(1)
N(1)-Cu(1)-N(1a)	180.0(1)	O(1a)-Cu(1)-N(1a)	85.2(1)
O(4)-Cu(1)-0(4a)	180.0(1)	O(4)-Cu(1)-N(1)	89.5(1)
Cu(1)-O(1)-C(1)	115.3(1)	Cu(1)-N(1)-C(2)	104.5(1)
Cu(1)-N(1)-C(3)	111.4(1)	C(2)-N(1)-C(3)	111.9(1)
Cu(1)-N(1)-C(6)	108.5(1)	C(2)-N(1)-C(6)	111.2(1)
C(3)-N(1)-C(6)	109.2(1)	O(1)-C(1)-O(2)	124.0(2)
O(1)-C(1)-C(2)	117.0(1)	O(2)-C(1)-C(2)	118.9(1)
N(1)-C(2)-C(1)	111.0(1)	N(1)-C(3)-N(2)	114.4(1)
C(3)-N(2)-C(4)	123.4(2)	O(3)-C(4)-N(2)	122.8(2)
O(3)-C(4)-C(5)	122.6(2)	N(2)-C(4)-C(5)	114.6(2)
N(1)-C(6)-N(3)	113.5(1)	C(6)-N(3)-C(7)	122.1(1)
O(4)-C(7)-N(3)	121.2(2)	O(4)-C(7)-C(8)	123.0(2)
N(3)-C(7)-C(8)	115.8(2)		

latter. The Cu(1)-O(1) and Cu(1)-N(1) bond lengths are comparable to those of *cis*-Cu(gly)$_2 \cdot H_2O$;[3] and the bond lengths in the glycinate moieties and the methylacetamido fragments are normal.[7–9]

In the crystal lattice, two water molecules of crystallization form several close intermolecular contacts as shown in Figure 1 and Table 4. The intermolecular contacts representing hydrogen bonds are shown in the unit cell packing diagram in Figure 2 and these link the $C_{16}H_{28}N_6O_8Cu$ molecules into a three-dimensional network.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters and observed and calculated structure factor amplitudes are available on request from the authors.

Table 4 Intermolecular contact distances

Bond	Distances (Å)	Symmetry operation
O(3)...O(1w)	2.863	
O(2w)...O(2)	2.788	
O(2w)...O(1w)$^{\#}$	2.745	$^{\#}$:1 + x,y,z
O(1w)...O(2w)*	2.703	*:x − 1, 0.5 − y, − 0.5 + z

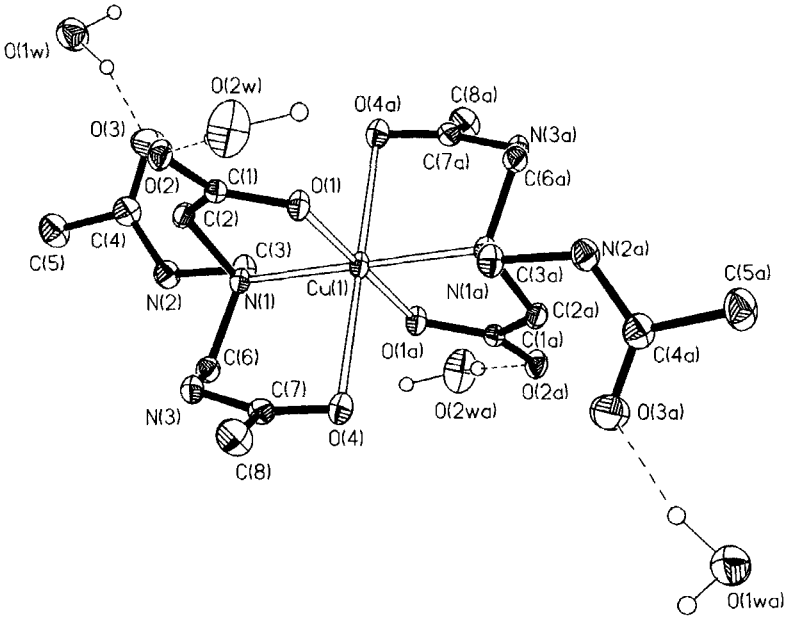

Figure 1 Molecular structure of $C_{16}H_{28}N_6O_8Cu \cdot 2H_2O$.

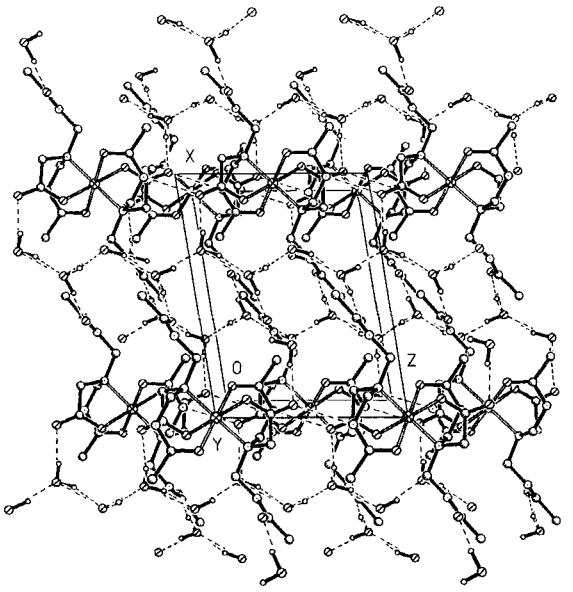

Figure 2 Diagram showing the unit cell contents projected on the *xz* plane. Hydrogen bonds are indicated by broken lines.

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