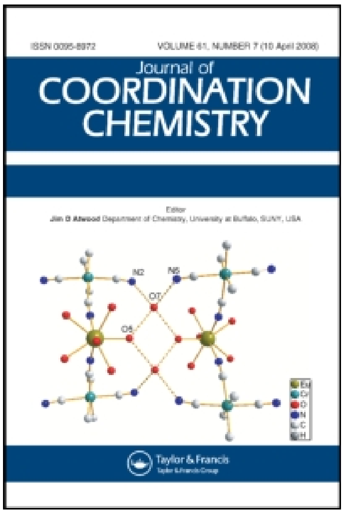

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AQUA*BIS*(*N*-HYDROXYMETHYL-*L*-PROLINATO)COPPER(II) FORMED BY THE *N*-HYDROXYMETHYLATION OF THE COPPER(II) CHELATE OF *L*-PROLINE

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AQUA*BIS*(*N*-HYDROXYMETHYL-*L*-PROLINATO)-COPPER(II) FORMED BY THE *N*-HYDROXYMETHYLATION OF THE COPPER(II) CHELATE OF *L*-PROLINE

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The reaction of bis(*L*-prolinato)copper(II) with formaldehyde results in the formation of the title compound which has been characterized by X-ray analysis and is found to possess a distorted square pyramidal geometry about the copper atom.

KEYWORDS: *bis*(*L*-prolinato) copper(II), formaldehyde, *N*-hydroxymethylation, X-ray structure

INTRODUCTION

Although condensations involving chelated α- and β-amino acids with formaldehyde have been extensively studied,[1–8] the products of such reactions involving cyclic amino acids have only been isolated recently.[9]

In the present study, we report the condensation of formaldehyde with the copper(II) chelate of the cyclic amino acid *L*-proline, which leads to *N*-hydroxymethylation of the metal(II) chelate. An X-ray crystallographic investigation of the product, aqua*bis*-(*N*-hydroxymethyl-*L*-prolinato)copper (II), has been performed and results are discussed herein.

EXPERIMENTAL

Reagents

L-proline was obtained from the B.D.H. Chemical Company. Formaldehyde was supplied by May and Baker as a 37% w/v aqueous solution.

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Bis(*L*-prolinato)copper(II) dihydrate, [Cu-(*L*-pro)$_2\cdot 2H_2O$], was prepared by a previously reported procedure.[10]

Preparation of bis(N-hydroxymethyl-L-prolinato) copper(II). $C_{12}H_{20}N_{20}N_2O_6Cu\cdot H_2O$

A reaction mixture consisting of Cu(*L*-pro)$_2\cdot 2H_2O$ (1.0 g, 0.003 mol) and 10cm^3 of a 37% w/v aqueous solution of formaldehyde (0.12 mol) was stirred thoroughly. The mixture was allowed to stand for a week at room temperature, whence blue crystals appeared. These were washed with an ethanol-acetone mixture and finally dried in the oven at 58°C overnight. Yield 0.3 g (27%). *Anal.:* Calcd. for $C_{12}H_{20}N_2O_6Cu\cdot H_2O$:C, 38.97; H, 5.99; N, 7.57%. Found: C, 38.79; H, 5.96; N, 7.38%.

Determination of the crystal structure of $C_{12}H_{20}N_2O_6Cu\cdot H_2O$

Intensity data for a flat blue crystal with dimensions 0.2 × 0.3 × 0.4 mm were measured at room temperature on a Siemens P4 diffractometer woth MoK$_\alpha$ radiation, $\lambda = 0.71073$Å. The $\Theta/2\Theta$ scan was employed to measure a total of 1694 reflections such that $\Theta_{max} \leq 27.5°$. No significant decomposition occured during data collection. Corrections were applied for Lorentz and polarization effects and for absorption.[11] There were 1540 unique data of which 1443 satisfied the criterion $F > 4.0\ \sigma(F)$ and these were used in subsequent analysis. Details of crystal data are listed in Table 1.

The structure was solved using direct methods[12] with the Seimens SHELXTL program (PC Version).[13] The structure was refined by full-matrix least-squares methods using 242 parameters. In the refinement, all non-hydrogen atoms were assigned anisotropic thermal parameters while hydrogen atoms were assigned isotropic thermal parameters. A weighting scheme of the form $W = [\sigma^2(F)+gF^2]^{-1}$ was used an refinement was contained to final $R = 0.030$, $R_w = 0.033$ for $g = 0.0009$. Atomic coordinates for non-hydrogen atoms are listes in Table 2, and bond lengths and angles in Table 3. The atom numbering scheme employed is shown in Figure 1, which was drawn with ORTEP.[14]

Table 1 Crystal data and refinement details for $C_{12}H_{20}N_2O_6Cu\cdot H_2O$.

Formula	$C_{12}H_{20}N_2O_6Cu\cdot H_2O$
Formula weight	405.9
Crystal system	Monoclinic
Space group	$P2_1$
a Å	7.3770(10)
*b*Å	12.372(2)
*c*Å	9.7320(0)
β°	101.690(0)
Z	2
ρ_c (g cm^{-3})	1.550
F (000)	426
μ ($^{-1}$)	13.0
Data collected	1694
Unique data	1540
Data with F>4.0$\sigma(F)$	1443
R	0.030
R_w	0.033

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å × 10^3)*.

	x/a	y/b	z/c	U_{eq}
Cu(1)	1859(1)	2946	8549(1)	29(1)
O(1)	2558(6)	1852(3)	7400(3)	37(1)
O(3)	1317(6)	4198(3)	9668(3)	39(1)
O(5)	- 264(7)	1923(3)	9308(4)	49(2)
N(1)	420(7)	3616(3)	6746(4)	31(2)
N(2)	4053(6)	2713(3)	10185(4)	28(2)
C(1)	1960(8)	1950(4)	6065(4)	33(2)
O(2)	2360(7)	1349(3)	5187(4)	53(2)
C(2)	582(8)	2853(6)	5584(4)	39(2)
C(3)	- 1378(13)	2442(8)	5047(10)	90(4)
C(4)	- 2521(14)	2837(11)	5978(11)	97(4)
C(5)	- 1587(9)	3801(5)	6698(5)	44(2)
C(6)	2271(8)	4256(4)	10906(4)	31(2)
O(4)	2049(6)	4965(3)	11752(4)	45(1)
C(7)	3678(8)	3377(4)	11388(4)	33(2)
C(8)	3044(12)	2592(5)	12362(6)	55(3)
C(9)	4039(19)	1576(7)	12178(9)	108(5)
C(10)	4240(9)	1557(4)	10677(5)	41(2)
C(11)	1334(11)	4664(4)	6570(6)	49(3)
O(6)	3229(8)	4492(5)	6802(5)	78(3)
C(12)	5655(8)	3088(6)	9680(4)	44(2)
C(7)	7328(5)	2944(5)	10657(4)	55(1)
O(8)	4428(7)	5068(5)	4451(4)	60(2)
C(9)	1594(8)	- 356(4)	7713(6)	71(2)

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

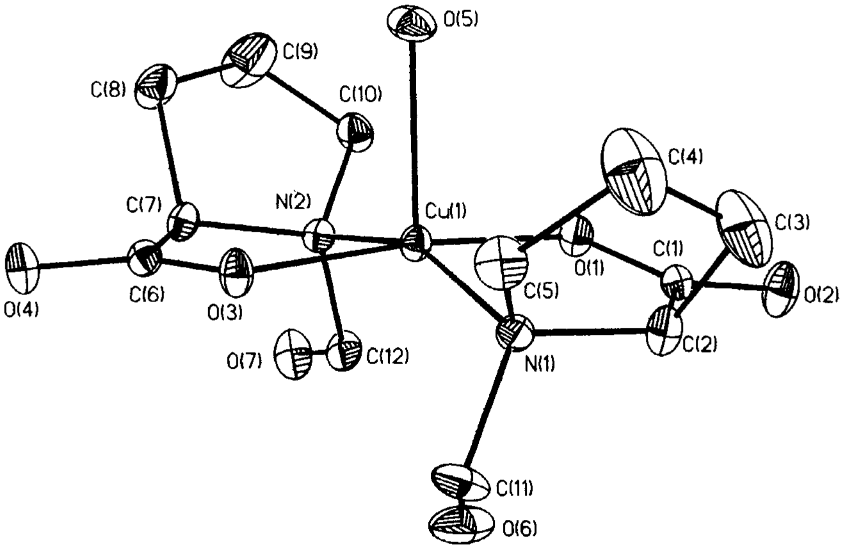

Figure 1 Molecular structure and atom numbering scheme employed for $C_{12}H_{20}N_2O_6Cu \cdot H_2O$.

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

Cu(1)-O(1)	1.893 (4)	Cu(1)-O(3)	1.980 (4)
Cu(1)-O(5)	2.2523 (5)	Cu(1)-N(1)	2.034 (4)
Cu(1)-N(2)	2.048 (4)	O(1)-C(1)	1.290 (5)
O(3)-C(6)	1.268 (5)	N(1)-C(2)	1.497 (7)
N(1)-C(5)	1.489 (8)	N(1)-C(11)	1.487 (7)
N(2)-C(12)	1.444 (8)	C(1)-O(2)	1.214 (6)
C(1)-C(2)	1.519 (8)	Cu(2)-C(3)	1.522 (11)
C(3)-C(4)	1.443 (16)	C(4)-C(5)	1.481 (14)
C(6)-O(4)	1.236 (6)	C(6)-C(7)	1.511 (8)
C(7)-C(8)	1.497 (9)	C(8)-C(9)	1.484 (13)
C(9)-C(10)	1.498 (11)	C(11)-O(6)	1.386 (10)
C(12)-O(7)	1.408 (6)		
O(1)-Cu(1)-O(3)	173.7(2)	O(1)-Cu(1)-O(5)	94.7(2)
O(3)-Cu(1)-O(5)	91.6(2)	O(1)-Cu(1)-N(1)	86.5(2)
O(3)-Cu(1)-N(1)	91.6(1)	O(5)-Cu(1)-N(1)	103.6(2)
O(1)-Cu(1)-N(2)	95.3(2)	O(3)-Cu(1)-N(2)	84.2(1)
O(5)-Cu(1)-N(2)	99.1(2)	N(1)-Cu(1)-N(2)	156.9(2)
Cu(1)-O(1)-C(1)	116.7(3)	Cu(1)-O(3)-C(6)	115.6(3)
Cu(1)-N(1)-C(2)	106.7(3)	Cu(1)-N(1)-C(5)	115.6(3)
C(2)-N(1)-O(5)	107.7(4)	Cu(1)-N(1)-C(11)	106.6(3)
C(2)-N(1)-C(11)	110.8(5)	C(5)-N(1)-C(11)	109.5(4)
Cu(1)-N(2)-C(7)	106.7(3)	Cu(1)-N(2)-C(10)	112.8(3)
C(7)-N(2)-C(10)	106.9(4)	Cu(1)-N(2)-C(12)	105.2(3)
C(7)-N(2)-C(12)	112.5(4)	C(10)-N(2)-C(12)	112.6(5)
O(1)-C(1)-O(2)	124.7(5)	O(1)-C(1)-C(2)	116.8(4)
O(2)-C(1)-C(2)	118.5(4)	N(1)-C(2)-C(3)	112.5(3)
N(1)-C(2)-C(3)	104.7(6)	C(1)-C(2)-C(3)	113.0(6)
C(2)-C(3)-C(4)	107.9(8)	C(3)-C(4)-C(5)	107.1(9)
N(1)-C(5)-C(4)	104.8(6)	O(3)-C(6)-O(4)	123.4(5)
O(3)-C(6)-C(7)	117.9(4)	O(4)-C(6)-C(7)	118.6(4)
N(2)-C(7)-C(6)	112.0(3)	N(2)-C(7)-C(8)	105.7(4)
N(6)-C(7)-C(8)	112.3(6)	C(7)-C(8)-C(9)	104.(7)
C(8)-C(9)-C(10)	106.3(6)	N(2)-C(10)-C(9)	105.9(5)
N(1)-C(11)-O(6)	108.3(5)	N(2)-C(12)-O(7)	113.3(4)

RESULTS AND DISCUSSION

The molecular structure of the reaction product, aqua*bis*(*N*-hydroxymethyl-*L*-prolinato)copper(II) (Figure 1) establishes the *N*-hydroxymethylation of Cu(L-pro)$_2 \cdot 2H_2O$ by formaldehyde. The two *L*-proline residues in the resultant complex are predictably *trans* with respect to each other.[2,15–19]

In the title compound, the copper atom is five-coordinate and exists in a distorted square pyramidal geometry with an N^2O_2 donor set of two *L*-proline ligands defining the basal plane and a coordinated water molecule in the axial position. The O(1), N(1), O(3) and N(2) atoms are coplanar within 0.15Å and the copper atom lies 0.2Å out of the idealised plane in the direction of the coordinated water molecule. As is characteristic of CU(II),[20–22] the bond to the apical water is longer than those to the donor atoms in the coordination square.

In the *L*-proline moiety, the atoms O(1), C(1), C(2) and N(1) of the chelate ring exhibit slight puckering and are coplanar within 0.05Å while the atoms of the pyrrolidine ring N(1), C(2), C(3), C(4), C(5) are coplanar to within 0.16Å. All the bond lengths within each L-proline are in the range observed for other comparable prolinato complexes.[10,23–25]

The formation of the title compound must necessitate the initial dissociation of the *N*-proton of each of the *L*-proline moieties, a fact corroborated by an earlier deuterium exchange study[26] which demonstrated the liability of the amino nitrogen proton of the chelated *L*-proline. Such lability for α- and β-amino acids is well known.[1–8]

The initial dissociation of the *N*-proton of the coordinated *L*-proline is followed by electrophilic attack by formaldehyde to give the *N*-hydroxymethyl species. Such *N*-hydroxymethylation of amino acid chelates is known to occur readily.[27]

Although the above *N*-hydroxymethylation is well documented, there is only one known case of an isolated stable product possessing an *N*-hydroxymethyl substituent.[6] The present compound represents the first instance of a crystallographic structural confirmation of an *N*-hydroxymethyl product obtained by the reaction of an amino acid chelate by formaldehyde.

Preliminary investigations show that the *bis*(*N*-hydroxymethyl-*L*-prolinato) copper (II) does not react further to give a similar *N,N'*-methylene bridged complex as occurs in the reactions of *bis*(4-hydroxy-*L*-prolinato)metal(II) with formaldehyde.[9]

SUPPLEMENTARY MATERIAL

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

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