

Reaction of Bis(glycinato)copper(II) with Formaldehyde and Benzaldehyde Phenylhydrazone: X-Ray Crystal Structure of Aquabis[(2,3,4,5-tetrahydro-2,6-diphenyl-1,2,4-triazin-4-yl)acetato-*O,N*⁴]copper(II) Dihydrate †

Soon-Beng Teo* and Siang-Guan Teoh

School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

Trevor W. Hambley and Michael R. Snow

Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001

The reaction of bis(glycinato)copper(II) with formaldehyde and benzaldehyde phenylhydrazone results in the formation of aquabis[2,3,4,5-tetrahydro-2,6-diphenyl-1,2,4-triazin-4-yl)acetato]-copper(II) dihydrate, $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$, which has been structurally characterized by X-ray diffraction studies. The compound crystallizes in the monoclinic space group *Cc*, with unit-cell dimensions $a = 35.222(9)$, $b = 6.126(4)$, $c = 15.986(7)$ Å, $\beta = 108.65(4)^\circ$, and $Z = 4$. The structure has been refined to $R = 0.073$ based on 1 128 independent observed reflections. The geometry about copper is grossly distorted octahedral with the two bidentate ligands occupying *cis* positions. A water molecule and a 'free' carboxyl oxygen atom from an adjacent ($x, y + 1, z$) cell complete the six-coordination for copper. The latter two oxygen donor atoms, which are also *cis*, are at greater distances from the Cu atom than the oxygen and nitrogen donors from L.

In 1960, Hahn¹ carried out an important reaction of the Mannich type between formaldehyde and glycine in the presence of a phenylhydrazone of an aryl aldehyde which established the reaction of the amino-acid nitrogen atom with formaldehyde. It has since been shown²⁻⁶ that such a reaction can still occur in an amino-acid complex. Recent studies^{7,8} have shown that, in the absence of base, formaldehyde reacts only with the amino-nitrogen of the α -amino acidatometal(II) complex while the α -carbon atom is unaffected. This behaviour contrasts with the base-catalysed reaction where both the nitrogen and α -carbon atoms of the chelated amino acid are attacked by formaldehyde.²⁻⁵ In view of the above findings, the reaction of bis(glycinato)copper(II) with formaldehyde and benzaldehyde phenylhydrazone was carried out in the absence of base and yielded aquabis[(2,3,4,5-tetrahydro-2,6-diphenyl-1,2,4-triazin-4-yl)acetato]copper(II) dihydrate $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$. The preparation and X-ray crystal structure of the complex are reported herein.

Experimental

Benzaldehyde phenylhydrazone and bis(glycinato)copper(II) were prepared according to previously reported procedures.⁴⁻¹¹ Reagent-grade chemicals were used in all instances.

Preparation of Aquabis[(2,3,4,5-tetrahydro-2,6-diphenyl-1,2,4-triazin-4-yl)acetato]copper(II) Dihydrate.—A 250-cm³ acetone-water mixture (2:1) containing bis(glycinato)copper(II) (2.2 g, 0.01 mol), formaldehyde (80 cm³ of 40% w/v solution, 1.0 mol), and benzaldehyde phenylhydrazone (4.0 g, 0.02 mol) was thoroughly stirred, filtered and then allowed to stand for 3 d at room temperature (pH of the mixture was 4.5).

The blue crystals which formed were filtered off, washed successively with cold distilled water, ethanol, and acetone and were finally dried under vacuum at 50 °C for 5 h. Yield 3.1 g

(44%) (Found: C, 57.6; H, 5.5; N, 11.9. $\text{C}_{34}\text{H}_{38}\text{CuN}_6\text{O}_7$, requires C, 57.8; H, 5.4; N, 11.9%).

Crystal Data.— $\text{C}_{34}\text{H}_{38}\text{CuN}_6\text{O}_7$, $M = 706.3$, monoclinic, space group *Cc*, $a = 35.222(9)$, $b = 6.126(4)$, $c = 15.986(7)$ Å, $\beta = 108.65(4)^\circ$, $U = 3\,268.2$ Å³ (by least-squares refinement of diffractometer setting angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.480$ g cm⁻³. Blue needle-shaped crystals. Crystal dimensions 0.25 × 0.03 × 0.03 mm, $\mu(\text{Mo-K}\alpha) = 6.94$ cm⁻¹, $F(000) = 758$.

Data Collection and Processing.—CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width ($^\circ$) $1.00 + 0.35\tan\theta$, aperture width (mm) $2.40 + 0.50\tan\theta$, graphite monochromated Mo- K_α radiation; 2 975 reflections measured ($1.0 \leq \theta \leq 22.0^\circ$, $+h, +k, \pm l$), 1 985 unique non-zero (merging $R = 0.016$). Lorentz, polarization, crystal decay (less than 2%), and absorption (min. 1.08 to max. 1.13) effects corrected for.

Structure Analysis and Refinement.—The structure was solved by heavy-atom methods; the location of the copper atom was determined by analysis of a Patterson map and this location was confirmed by direct methods. The copper atom lies very close to what is a centre of symmetry in the space group *C2/c* and the benzaldehyde phenylhydrazone portions of the ligands are close to being centrosymmetrically related. Thus, there is some ambiguity as to whether the structure is centric or non-centric. *E*-Value statistics suggest a non-centric structure but not clearly so. We adopted the non-centric choice *Cc* for reasons which will be outlined below.

Hydrogen atoms were included at calculated sites (C-H, 0.97 Å) with a group thermal parameter. Only the copper atom was refined anisotropically. Full-matrix least-squares refinement converged with $R [= \sum(|F_o| - |F_c|)/\sum|F_o|] = 0.073$, $R' = 0.076$ [weighting scheme of the form $2.24/\sigma^2 F_o = 0.005 F_o^2$], for 1 128 reflections with $I > 2.5\sigma(I)$. Maximum peaks in a final difference map were less than ± 0.6 e Å⁻³.

Scattering factors (Cu⁰ for Cu^{II}) and anomalous dispersion terms were taken from International Tables.¹² All calculations were carried out using SHELX-76,¹³ ORTEP,¹⁴ and data reduction programs¹⁵ implemented on a CYBER computer. Final atomic co-ordinates are listed in Table 1 and bond lengths and angles in Table 2.

† Supplementary data available (No. SUP 56415, 4 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

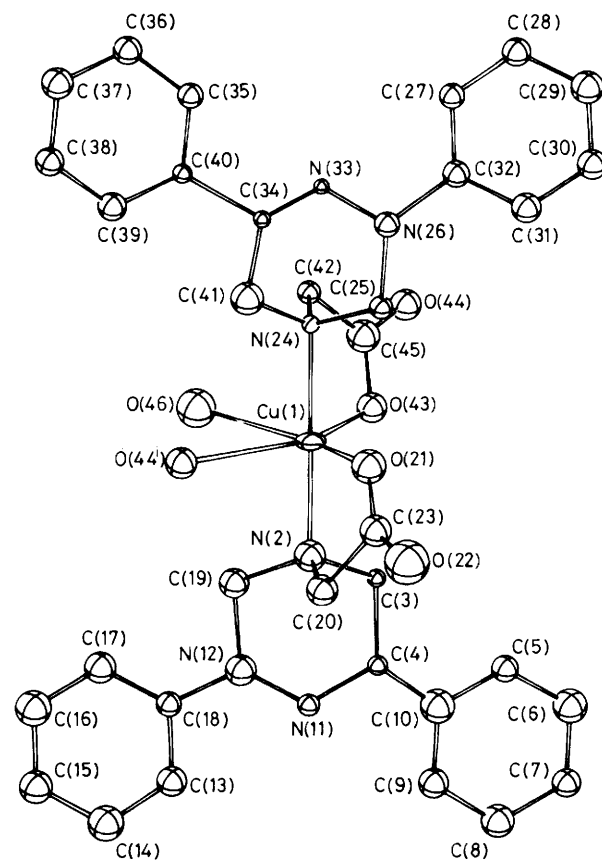
Atom	x	y	z	Atom	x	y	z
Cu(1)	5 000	4 952(13)	5 000	C(25)	5 703(9)	6 913(54)	4 818(20)
N(2)	4 423(11)	3 784(64)	4 479(23)	N(26)	6 134(8)	7 747(42)	5 128(28)
C(3)	4 135(9)	5 630(44)	4 037(20)	C(27)	6 664(7)	10 629(47)	5 268(13)
C(4)	3 709(8)	4 683(52)	3 607(27)	C(28)	6 800(7)	12 476(47)	4 955(13)
C(5)	3 496(5)	7 600(44)	2 630(27)	C(29)	6 557(7)	13 529(47)	4 210(13)
C(6)	3 205(5)	8 688(44)	1 969(27)	C(30)	6 176(7)	12 735(47)	3 778(13)
C(7)	2 820(5)	7 842(44)	1 648(27)	C(31)	6 040(7)	10 887(47)	4 092(13)
C(8)	2 728(5)	5 908(44)	1 987(27)	C(32)	6 283(7)	9 834(47)	4 837(13)
C(9)	3 019(5)	4 820(44)	2 648(27)	N(33)	1 392(6)	1 826(33)	5 832(13)
C(10)	3 403(5)	5 666(44)	2 969(27)	C(34)	6 278(8)	5 441(56)	6 199(28)
N(11)	3 599(9)	2 826(57)	3 971(20)	C(35)	6 955(7)	5 378(39)	7 394(13)
N(12)	3 848(9)	1 854(58)	4 678(20)	C(36)	7 256(7)	4 542(39)	8 110(13)
C(13)	3 378(7)	-814(41)	4 691(14)	C(37)	7 200(7)	2 571(39)	8 479(13)
C(14)	3 266(7)	-2 728(41)	5 010(14)	C(38)	6 845(7)	1 435(39)	8 133(13)
C(15)	3 510(7)	-3 620(41)	5 793(14)	C(39)	6 544(7)	2 270(39)	7 417(13)
C(16)	3 866(7)	-2 598(41)	6 258(14)	C(40)	6 599(7)	4 242(39)	7 048(13)
C(17)	3 977(7)	-684(41)	5 939(14)	C(41)	5 866(13)	4 548(74)	6 028(37)
C(18)	3 733(7)	207(41)	5 155(14)	C(42)	5 547(8)	7 853(43)	6 105(29)
C(19)	4 253(9)	2 834(50)	5 205(28)	O(43)	4 877(5)	8 096(39)	5 099(13)
C(20)	4 455(9)	2 123(50)	3 779(28)	O(44)	5 151(6)	11 295(34)	5 722(14)
O(21)	5 049(7)	4 141(34)	3 933(15)	C(45)	5 167(11)	9 214(55)	5 657(23)
O(22)	4 781(9)	2 089(59)	2 656(23)	O(46)	5 043(7)	4 755(59)	6 584(15)
C(23)	4 805(9)	3 008(52)	3 404(22)	O(47)	5 112(10)	-1 350(68)	2 360(23)
N(24)	5 588(8)	6 104(41)	5 531(28)	O(48)	4 763(27)	7 039(94)	2 500(47)

Discussion

The structure determination establishes that condensation of formaldehyde and benzaldehyde phenylhydrazone has occurred on the chelated glycine, resulting in a bidentate ligand with one oxygen and one nitrogen donor. An ORTEP plot of the complex is shown in the Figure. The co-ordination sphere is made up of two bidentate ligands, a water molecule, and a 'free' carboxyl oxygen atom from an adjacent ($x, y + 1, z$) unit cell. Thus the structure consists of polymeric chains.

The geometry about copper is grossly distorted octahedral with the two bidentate ligands occupying *cis* positions. Bond lengths to the oxygen and nitrogen donors are apparently normal for copper(II) complexes.^{2,3,16} The water and 'free' carboxyl oxygen atoms, which are also *cis*, are at a greater distance (*ca.* 2.5 Å) from the central copper atom. Such extended distances are typical of (4 + 2)-*trans*-copper(II) complexes.^{17,18} The only other example of two long bonds in *cis* positions are the copper-thioether bonds in the recently reported structure of [1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane]dichloro-copper(II).¹⁹ The present result could be considered as an averaged ligand field of four oxygen atoms constituting a very irregular square plane which could arise as a constraint on the O(44') position of the other molecule.^{17,20} We are reminded that copper(II) complexes do not have to undergo tetragonal distortions,^{17,21} especially where there are several different types of ligating atoms. In the present case the extension of the O(44')-Cu and O(46)-Cu bond lengths leads to a closing up of the O(46)-Cu-O(44') angle and an opening up of the O(21)-Cu-O(43) angle.

An alternative description of the copper geometry is possible if the centrosymmetric space group $C2/c$ is adopted. In that case the copper lies on a centre of symmetry with the benzaldehyde phenylhydrazone moieties related across the centre. The acetate moieties as described above are, however, not related by the centre and a disordered model is necessary with two contributors present at half occupancy. Two descriptions of the geometry are then possible; the *cis* arrangement as described above or a more usual *trans* arrangement of the acetate moieties. However, this latter arrangement, being centro-

**Figure.** Molecular structure of $[\text{Cu}(\text{L})_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$

symmetric, is not consistent with the co-ordination of both water and 'free' carboxyl oxygens and therefore requires a breakdown in space group symmetry. Refinement, carried out in

Table 2. Bond lengths (Å) and angles (°)

N(2)–Cu(1)	2.062(37)	O(21)–Cu(1)	1.838(22)
N(24)–Cu(1)	2.093(25)	O(43)–Cu(1)	1.991(19)
O(44 ¹)–Cu(1)	2.498(20)	O(46)–Cu(1)	2.491(20)
C(3)–N(2)	1.533(43)	C(19)–N(2)	1.576(39)
C(20)–N(2)	1.543(40)	C(4)–C(3)	1.548(38)
C(10)–C(4)	1.365(33)	N(11)–C(4)	1.388(38)
N(12)–N(11)	1.329(35)	C(18)–N(12)	1.401(36)
C(19)–N(12)	1.529(38)	C(23)–C(20)	1.627(38)
C(23)–O(21)	1.213(31)	C(23)–O(22)	1.299(39)
C(25)–N(24)	1.416(32)	C(41)–N(24)	1.415(46)
C(42)–N(24)	1.447(34)	N(26)–C(25)	1.526(36)
C(32)–N(26)	1.512(33)	C(40)–C(34)	1.637(31)
C(41)–C(34)	1.492(48)	C(45)–C(42)	1.546(42)
C(45)–O(43)	1.313(36)	C(45)–O(44)	1.282(30)
O(48)–O(47)	1.644(57)		
O(21)–Cu(1)–N(2)	84.5(12)	N(24)–Cu(1)–N(2)	179.4(17)
N(24)–Cu(1)–O(21)	95.3(10)	O(43)–Cu(1)–N(2)	99.0(12)
O(43)–Cu(1)–O(21)	115.0(9)	O(43)–Cu(1)–N(24)	81.6(9)
O(44 ¹)–Cu(1)–N(2)	85.0(11)	O(44 ¹)–Cu(1)–N(24)	94.4(10)
O(44 ¹)–Cu(1)–O(27)	96.7(11)	O(44 ¹)–Cu(1)–O(46)	63.4(13)
O(46)–Cu(1)–N(2)	97.2(11)	O(46)–Cu(1)–N(27)	82.7(12)
C(3)–N(2)–Cu(1)	110.6(24)	C(19)–N(2)–Cu(1)	112.8(21)
C(19)–N(2)–C(3)	105.1(28)	C(20)–N(2)–Cu(1)	103.3(22)
C(20)–N(2)–C(3)	110.1(25)	C(20)–N(2)–C(19)	115.0(29)
C(4)–C(3)–N(2)	109.4(24)	C(10)–C(4)–C(3)	126.0(26)
N(11)–C(4)–C(3)	118.8(23)	N(11)–C(4)–C(10)	114.5(25)
C(5)–C(10)–C(4)	116.2(16)	C(9)–C(10)–C(4)	123.8(16)
N(12)–N(11)–C(4)	121.7(28)	C(18)–N(12)–N(11)	124.0(28)
C(19)–N(12)–N(11)	122.6(27)	C(19)–N(12)–C(18)	111.3(22)
C(13)–C(18)–N(12)	113.8(15)	C(17)–C(18)–N(12)	125.0(15)
N(12)–C(18)–N(12)	104.2(22)	C(23)–C(20)–N(2)	106.7(24)
C(23)–O(21)–Cu(1)	123.1(23)	O(21)–C(23)–C(20)	112.6(28)
O(22)–C(23)–C(20)	111.1(28)	O(22)–C(23)–O(21)	135.5(34)
C(25)–N(24)–Cu(1)	107.0(19)	C(41)–N(24)–Cu(1)	114.7(23)
C(41)–N(24)–C(25)	111.3(27)	C(42)–N(24)–Cu(1)	102.8(17)
C(42)–N(24)–C(25)	111.3(23)	C(42)–N(24)–C(41)	109.5(25)
N(26)–C(25)–N(24)	111.5(23)	C(32)–N(26)–C(25)	126.3(23)
C(27)–C(32)–N(26)	121.4(12)	C(31)–C(32)–N(26)	118.5(12)
C(41)–C(34)–C(40)	111.1(25)	C(35)–C(40)–C(34)	113.8(11)
C(39)–C(40)–C(34)	126.2(11)	C(34)–C(41)–N(24)	108.3(32)
C(45)–C(42)–N(24)	110.6(23)	C(45)–O(43)–Cu(1)	114.7(19)
O(43)–C(45)–C(42)	113.8(27)	O(44)–C(45)–C(42)	123.5(32)
O(44)–C(45)–O(43)	122.0(33)		

the non-centric space group *Cc*, was complicated by the appearance, as expected, of a centrically imaged set of atoms. Choice of a logical and connected set of atoms resulted in the almost complete disappearance of the imaged set. Thus it appears that the adopted, non-centric, model is correct.

Unfortunately, the accuracy of the structure is limited because of small crystal size and because of refinement problems arising from the aforementioned pseudosymmetry problems. All bond lengths and angles within the complex appear to be typical of such compounds.^{2,3,16} Bond lengths and angles defining the co-ordination spheres are given in Table 2.

The water molecules present in the lattice, O(47) and O(48), are present at occupancies of 69(3) and 44(4)% respectively. Both are involved in apparent weak hydrogen bonds.

The formation of the title compound must necessarily involve the initial loss of protons from the nitrogen atom of

bis(glycinato)copper(II), a phenomenon which has been well documented.²² This step leads to electrophilic attack, on the nitrogen atom, by formaldehyde molecules followed by subsequent condensation with benzaldehyde phenylhydrazone resulting in the formation of a heterocyclic triazine ring structure. In this reaction the α -carbon atom of the co-ordinated glycine is unaffected by formaldehyde attack, similar to a recent reaction of formaldehyde with bis(glycinato)zinc(II) in the absence of base.⁷

Acknowledgements

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