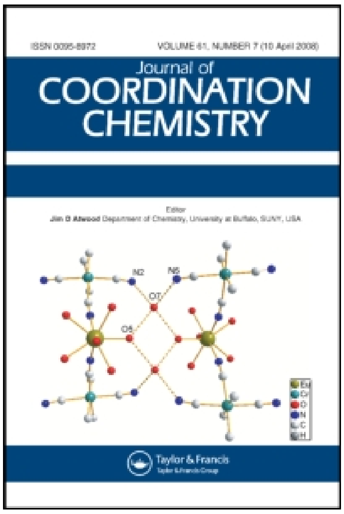


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Reaction of Bis(β-Alaninato)Copper(II) with Formaldehyde and Ammonia: X-Ray Crystal Structure of [3N,7N-(1,3,5,7-Tetraazabicyclo-[3.3.1]Nonyl)-DI-3-Propionato]Copper(II)

Soon-Beng Teo[a]; Chew-Hee Ng[a]; Siang-Guan Teoh[a]; Hoong-Kun Fun[b]
[a] School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia [b] X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, Penang, Malaysia

To cite this Article Teo, Soon-Beng , Ng, Chew-Hee , Teoh, Siang-Guan and Fun, Hoong-Kun(1991) 'Reaction of Bis(β-Alaninato)Copper(II) with Formaldehyde and Ammonia: X-Ray Crystal Structure of [3N,7N-(1,3,5,7-Tetraazabicyclo-[3.3.1]Nonyl)-DI-3-Propionato]Copper(II)', Journal of Coordination Chemistry, 24: 2, 151 — 158

To link to this Article: DOI: 10.1080/00958979109409457

URL: http://dx.doi.org/10.1080/00958979109409457

J. Coord. Chem. 1991, Vol. 24. pp. 151–158
Reprints available directly from the publisher
Photocopying permitted by license only

REACTION OF BIS(β-ALANINATO)COPPER(II) WITH FORMALDEHYDE AND AMMONIA: X-RAY CRYSTAL STRUCTURE OF [3N,7N-(1,3,5,7-TETRAAZABICYCLO-[3.3.1]NONYL)-DI-3-PROPIONATO]COPPER(II)

SOON-BENG TEO,* CHEW-HEE NG, SIANG-GUAN TEOH

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

and HOONG-KUN FUN

X-ray Crystallography Laboratory, School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

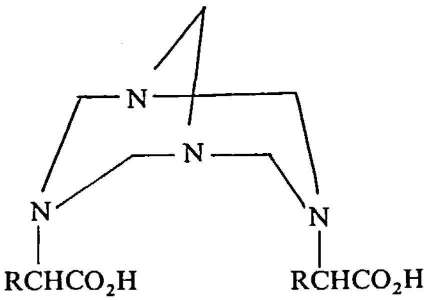
(Received October 29, 1990)

The reaction of bis(β-alaninato)copper(II) with formaldehyde and ammonia over the pH range 6.6–8.8 results in the formation of [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)-di-3-propionato]copper(II) trihydrate, $C_{11}H_{24}N_4O_7Cu$, which crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.903(2)$, $b = 7.340(2)$, $c = 19.435(3)$ Å, $\beta = 98.27(1)°$ and $Z = 4$. The structure has been refined to $R = 0.040$ and $R_w = 0.044$ based on 2655 reflections with $I \geq 2.5\sigma(I)$. The chelate molecules are linked in chains by a carbonyl oxygen to copper interaction which results in square pyramidal coordination of the copper ion.

Keywords: β-alanine, formaldehyde, ammonia, X-ray structure

INTRODUCTION

While the reactions of metal chelates of α-amino acids with formaldehyde have been extensively investigated[1–6] there has hitherto been no account of such reactions involving metal chelates of β-amino acids. Recent studies[7,8] have shown that the metal(II) chelates of glycine and α-alanine react with formaldehyde and ammonia to give the metal(II) complexes of 1 where R = H and CH_3, respectively.



1

---

* Author for correspondence.

In this paper we report the reaction of bis(β-alaninato)copper(II) with formaldehyde and ammonia which leads to the formation of [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)-di-3-propionato]copper(II). A full X-ray structural analysis of the compound has been carried out.

EXPERIMENTAL

Reagents

β-Alanine was supplied by 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 as described previously.[9]

Preparation of [3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)-di-3-propionato] copper(II)trihydrate, $C_{11}H_{18}N_4O_4Cu.3H_2O$

A reaction mixture consisting of Cu(β-ala)$_2$.4H$_2$O (1.0 g, 0.003 mol) and 10 cm^3 of a 37% w/v solution of formaldehyde (0.12 mol) was stirred thoroughly and its pH adjusted to 7.6 by the slow addition of concentrated ammonia solution. On standing for a week, deep blue crystals appeared. These were filtered and washed with acetone and were finally dried *in vacuo* for 3 h. Yield 1.0 g (83%). *Anal.*: Calcd. for $C_{11}H_{24}N_4O_7Cu$: C, 34.06; H, 6.24; N, 14.44%. Found: C, 43.50; H, 6.08; N, 14.21%. Although the reaction was carried out at pH 7.6, it was found that the same compound was isolated when the reaction was carried out in the pH range 6.6–8.8.

Determination of crystal structure of $C_{11}H_{18}N_4O_4Cu.3H_2O$

Intensity data for a crystal with dimensions 0.2 x 0.3 x 0.4 mm were measured at room temperature on a Syntex $P2_1$ diffractometer fitted with MoK_α radiation, λ = 0.71069 Å. The θ/2θ scan was employed to measure a total of 3495 reflections such that $\theta_{max} \leqslant 26°$. No significant decomposition occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption; max. and min. correction factors were 0.918 and 0.714 respectively.[10] There were 3071 unique data of which 2655 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and these were used in the subsequent analysis. Crystal data are listed in Table I.

The structure was solved using SHELX86[11] and refined by a full-matrix least-squares procedure based on F using SHELX76.[12] All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in their idealized positions (C–H = 0.96 Å) and refined isotropically. A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was used and the refinement continued to final $R = 0.040$, $R_w = 0.044$ for $k = 2.3$ and $g = 0.006$. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.79 e Å^{-3}. Fractional atomic coordinates are listed in Table II and the numbering scheme employed is shown in Figure 1, which was drawn with ORTEP.[13] The scattering factors for neutral Cu (corrected for f' and f'') were from ref. 14 and those for the remaining atoms were as incorporated in SHELX76.

TABLE I
Crystal data and refinement details for $C_{11}H_{24}N_4O_7Cu$.

Formula	$C_{11}H_{24}O_7Cu$
Formula weight	387.88
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.903(2)
b (Å)	7.340(2)
c (Å)	19.435(3)
β (°)	98.27(1)
v (A^3)	1511.0
Z	4
ρ_c ($g\,cm^{-3}$)	1.705
$F(000)$	812
μ(cm^{-1})	14.9
Data collected	3495
Unique data	3071
Data with $I \geq 2.5\,\rho(I)$	2655
R	0.040
R_w	0.044

TABLE II
Atomic coordinates ($\times 10^5$ for Cu; $\times 10^4$ for other atoms) and B_{eq}(A^2) values with e.s.d's in parentheses; $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$.

	x/a	y/b	z/c	B_{eq}
Cu1	11503(2)	8862(4)	15035(1)	1.62
O1	−233(2)	1485(3)	792(1)	2.23
C1	−278(2)	2206(3)	188(1)	1.87
O2	−1261(2)	2396(3)	−204(1)	3.01
C2	925(3)	2815(4)	−44(1)	2.54
C3	1872(2)	3567(4)	523(2)	2.30
N1	2449(2)	2198(3)	1039(1)	1.70
C4	3186(2)	827(3)	689(1)	2.05
C5	3332(2)	3235(3)	1567(1)	2.08
N2	3965(2)	−305(3)	1184(1)	2.16
N3	4124(2)	2055(3)	2038(1)	2.17
C6	4811(2)	858(4)	1634(2)	2.40
C7	3301(2)	−1456(4)	1602(1)	2.16
C8	3460(3)	976(4)	2485(1)	2.17
N4	2593(2)	−403(3)	2089(1)	1.80
C9	2198(2)	−1733(4)	2593(2)	2.87
C10	1197(3)	−1011(5)	2980(2)	3.04
C11	−58(3)	−1057(4)	2535(2)	2.36
O3	−123(2)	−499(3)	1904(1)	2.77
O4	−974(2)	−1647(3)	2768(1)	3.15
O1W	3471(3)	7800(4)	4619(2)	4.88
O2W	5736(3)	8624(4)	5746(2)	5.26
O3W	2652(2)	4332(4)	3771(1)	3.94

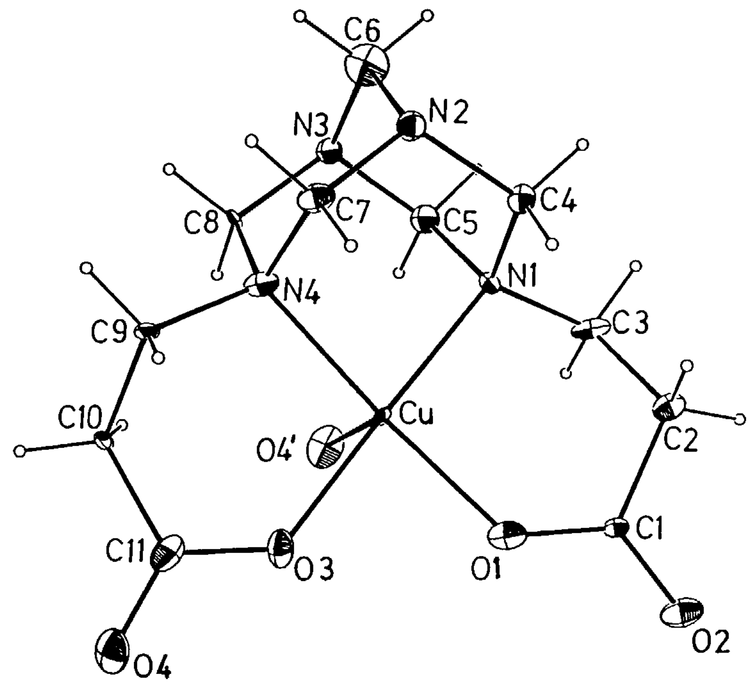


FIGURE 1 Molecular structure and numbering scheme employed for $[Cu(C_{11}H_{24}N_4O_7)]_n$.

RESULTS AND DISCUSSION

The molecular structure of the reaction product (Figure 1) established the condensation of formaldehyde with ammonia leading to the formation of a pentamethylenediamine group which bridges the two chelated β-alanine moieties; the overall structure is akin to hexamine. The two β-alanine residues in the resultant complex are *cis* with respect to each other which implies that the initial *trans* $Cu(\beta\text{-ala})_2.4H_2O$[9] must have undergone rearrangement to give the observed *cis* ligand configuration in the final product. Such *trans* → *cis* conversion in the configuration of the ligands is rather rare as reactions of amino acid complexes with aldehydes have always resulted in the *trans* metal-containing product, regardless of whether the starting ligands are *cis* or *trans*.[1-6] In fact, the only previous examples of such a phenomenon have involved the products of similar reactions of formaldehyde and ammonia with the metal(II) chelates of glycine and α-alanine, respectively.[7-8]

In the complex, the copper atom is five-coordinated and exists in a distorted square pyramidal environment, the basal plane being defined by two oxygen atoms and two nitrogen atoms derived from the β-alanine residues. All bond lengths within the ligand are in the range observed for similar complexes[9,15,16] and the Cu–N1,N4 and Cu–O1,O3 bond lengths are also typical (Table III).[2,4,9,15,16] The copper atom lies 0.17(1) Å out of the N_2O_2 basal plane (deviations from the least-squares are plane O1 −0.11(2); N1 0.10(2), N4 −0.10(2); O3 0.11(2) Å) in the direction of O4 (related by the symmetry operation $-x, \frac{1}{2}+y, \frac{1}{2}-z$), which occupies the axial position such that an infinite polymeric chain is generated, in the *b* axis direction, as highlighted in

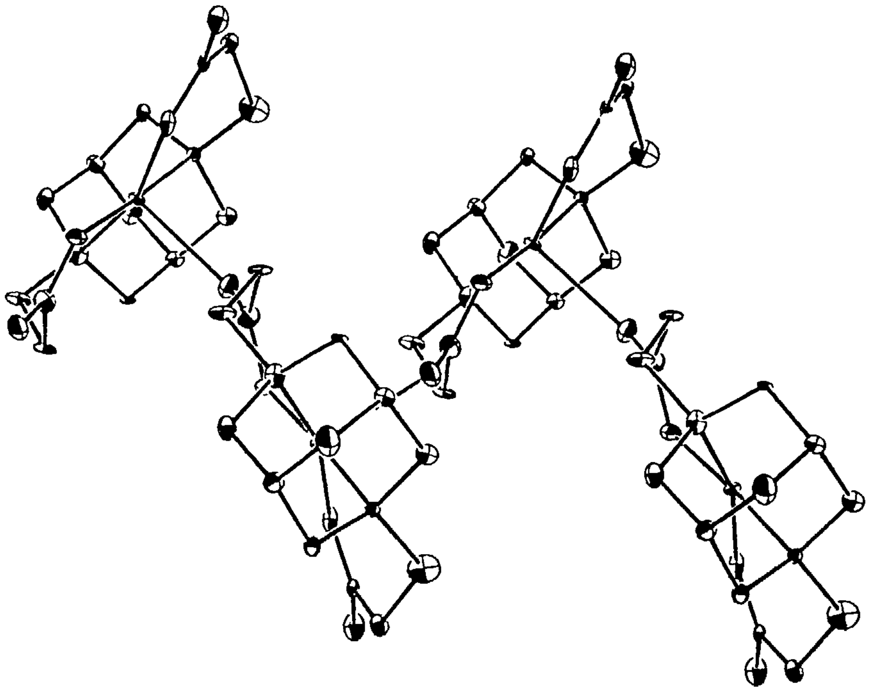
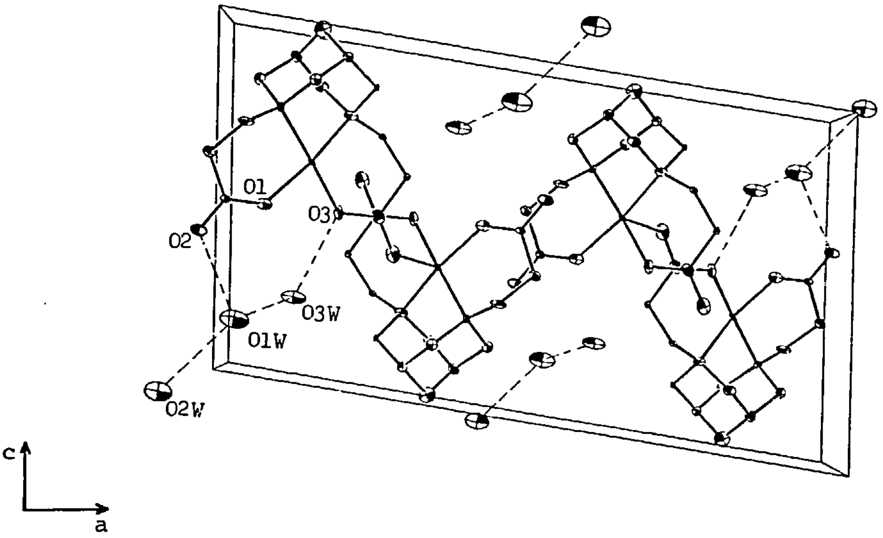


FIGURE 2 Diagram showing the polymeric nature of $[Cu(C_{11}H_{24}N_4O_7)]_n$ in the solid state.



GURE 3 Diagram showing the unit cell contents projected on the *ac* plane. Hydrogen bonds are licated by broken lines.

Figure 2. A similar polymeric structure is also found in the copper complex obtained from the reaction of bis(α-alaninato)copper(II) with formaldehyde and ammonia.[8] In this compound the copper atom lies 0.364(4) Å above the basal plane. The fact that the copper atom in the present complex lies nearer to the basal plane may be ascribed to the six-membered chelates formed by the β-alanine moieties (*c.f.* five-membered chelates of the α-alanine analogue) which allow more room for the metal to attain its idealized geometry.

TABLE III

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

O1–Cu1	1.944(2)	N1–Cu1–O1	95.5(1)
N1–Cu1	2.029(2)	N4–Cu1–O1	163.7(1)
N4–Cu1	2.036(2)	N4–Cu1–N1	86.4(1)
O3–Cu1	1.969(2)	O3–Cu1–O1	83.1(1)
O4′–Cu1	2.323(2)	O3–Cu1–N1	176.3(1)
C1–O1	1.281(3)	O3–Cu1–N4	94.0(1)
O2–C1	1.231(3)	C1–O1–Cu1	131.9(2)
C2–C1	1.515(4)	O2–C1–O1	122.0(2)
C3–C2	1.503(4)	C2–C1–O1	118.3(2)
N1–C3	1.493(3)	C2–C1–O2	119.7(2)
C4–N1	1.509(3)	C3–C2–C1	114.9(2)
C5–N1	1.509(3)	N1–C3–C2	115.1(2)
N2–C4	1.449(3)	C3–N1–Cu1	111.4(1)
N3–C5	1.452(3)	C4–N1–Cu1	109.5(1)
C6–N2	1.453(3)	C4–N1–C3	110.3(2)
C7–N2	1.439(3)	C5–N1–Cu1	110.7(1)
C6–N3	1.456(3)	C5–N1–C3	106.5(2)
C8–N3	1.444(3)	C5–N1–C4	108.3(2)
N4–C7	1.516(3)	N2–C4–N1	112.6(2)
N4–C8	1.517(3)	N3–C5–N1	113.1(2)
C9–N4	1.490(3)	C6–N2–C4	108.8(2)
C10–C9	1.509(4)	C7–N2–C4	114.6(2)
C11–C10	1.510(4)	C7–N2–C6	109.4(2)
O3–C11	1.285(4)	C6–N3–C5	108.9(2)
O4–C11	1.232(3)	C8–N3–C5	113.7(2)
		C8–N3–C6	109.6(2)
		N3–C6–N2	110.4(2)
		N4–C7–N2	113.3(2)
		N4–C8–N3	113.0(2)
		C7–N4–Cu1	108.1(1)
		C8–N4–Cu1	110.4(2)
		C8–N4–C7	108.7(2)
		C9–N4–Cu1	113.5(2)
		C9–N4–C7	107.3(2)
		C9–N4–C8	108.8(2)
		C10–C9–N4	113.3(2)
		C11–C10–C9	111.6(3)
		O3–C11–C10	117.4(2)
		O4–C11–C10	120.9(3)
		O4–C11–O3	121.8(3)
		C11–O3–Cu1	126.7(2)

O4′ is related by the symmetry operation $-x$, $1/2 + y$, $1/2 - x$.

The three lattice water molecules form several close intermolecular contacts as shown in Table IV. The intermolecular contacts representing hydrogen bonds are partly shown in the unit cell packing diagram in Figure 3 and these link the polymeric chains into an intricate three-dimensional network.

TABLE IV
Intermolecular contact distances.

Bond	Distance (Å)	Symmetry operation
O2W–O1W	3.116	x, y, z
O3W–O1W	3.093	x, y, z
O2W–O1W′	2.884	$-x, 2-y, -z$
O2–O1W″	2.824	$-x, y-1/2, 1/2-z$
O3W–O2W′	2.864	$1-x, 1-y, 1-z$
N2–O2W″	3.295	$x, 1/2-y, z-1/2$
O1–O3W′	3.289	$-x, y-1/2, 1/2-z$
O3–O3W′	2.881	$-x, y-1/2, 1/2-z$
O4–O3W′	3.352	$-x, y-1/2, 1/2-z$

Previous work[7,8] on the reactions of α-amino acid chelates with formaldehyde and ammonia at pH ≈ 8.5 has also yielded hexamine-like compounds, but on lowering the pH, metal(II) complexes having oxazolidine rings are obtained. In the present reaction, however, no such bis(oxazolidine)metal(II) complexes have been isolated. This observation is in accord with Gillard's[17] deuterium exchange studies which demonstrated the failure of the methylene protons in β-alanine to deuterate even at fairly high pH values.

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.

REFERENCES

1. A. Pasini and L. Casella, *J. Inorg. Nucl. Chem.*, **36**, 2133 (1974).
2. J.R. Brush, R.J. Magee, M.J. O'Connor, S.B. Teo, R.J. Geue and M.R. Snow, *J. Am. Chem. Soc.*, **95**, 2034 (1973).
3. S.B. Teo, S.G. Teoh, J.R. Rodgers and M.R. Snow, *J. Chem. Soc., Chem. Comm.*, 141 (1982).
4. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta.*, **107**, 211 (1985).
5. S.B. Teo, S.G. Teoh, T.W. Hambley and M.R. Snow, *J. Chem. Soc., Chem. Comm.*, 553 (1986).
6. S.B. Teo and M.J. O'Connor, *Inorg. Chim. Acta.*, **70**, 107 (1983).
7. S.B. Teo, S.G. Teoh and M.R. Snow, *Inorg. Chim. Acta.*, **85**, L1 (1984).
8. S.B. Teo, C.H. Ng and E.R.T. Tiekink, *Inorg. Chim. Acta.*, **163**, 129 (1988).
9. Y. Mitsui, Y. Iitaka and S. Sakaguchi, *Acta. Cryst.*, **B32**, 1634 (1976).
10. G. Ugozzoli, 'ABSORB', *A Computer Program for Correcting Observed Structure Factors from Absorption Effects in Crystal Structure Analysis, Comput Chem.*, Vol. II, **2**, (1987), pp. 109–120.
11. G.M. Sheldrick, 'SHELX-86', *A Program for Crystal Structure Determination*, (University of Gottingen, Federal Republic of Germany, 1986).
12. G.M. Sheldrick, 'SHELX-76', *A Program for Crystal Structure Determination and Refinement*, (University of Cambridge, England, 1976).

13. C.K. Johnson, *ORTEP*, report ORNL-3794, Oak Ridge National Laboratory, Tenessee, U.S.A.
14. *International Tables for X-ray Crystallography*, Vol. IV, (Kynoch Press, Birmingham, 1974).
15. K. Tomita, *Bull. Chem. Soc. Japan*, **34**, 297 (1961).
16. H.C. Freeman, *Adv. Protein Chem.*, **22**, 257 (1967).
17. R.D. Gillard and D.A. Phipps, *J. Chem. Soc., Chem. Comm.*, 800 (1970).