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Condensation of Bis(L-alaninato)copper(II) with Formaldehyde: X-ray Crystal Structure of [3*N*,7*N*-(1,3,5,7-Tetraazabicyclo[3.3.1]nonyl)-dipropionato]copper(II)

SOON-BENG TEO*, CHEW-HEE NG

School of Chemical Sciences, University Sains Malaysia, Penang (Malaysia)

and EDWARD R. T. TIEKINK*

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, S.A. 5001 (Australia)

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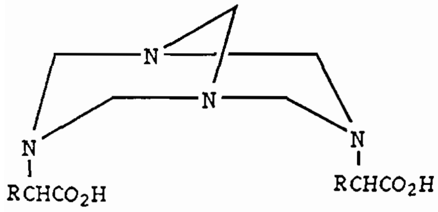
It is known that under appropriate conditions the formaldehyde–ammonia reaction leads quantitatively to hexamine [1–3]. Recently [4, 5] it has been found that at pH 8.5 the reactions of bis(glycinato)-metal(II) complexes with formaldehyde and ammonia result in the formation of the metal(II) complexes of 3*N*,7*N*-(1,3,5,7-tetraazabicyclo[3.3.1]-nonyl)diacetic acid (**1**) (R = H).



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In this communication, we report the reaction of bis(L-alaninato)copper(II), Cu(L-ala)$_2$, with formaldehyde and ammonia at pH 8.5 which gives rise to formation of the copper(II) complex of **1** (R = CH_3). The characterization of the product by single-crystal X-ray diffractometry is also reported.

It has been demonstrated that in the base-catalyzed reactions of α-amino acidato copper(II) complexes with formaldehyde [6–9], the initial attack by the latter on the α-carbon and nitrogen atoms of the former and the subsequent condensation of the hydroxymethyl groups so formed give rise to complexes having oxazolidine rings. In fact at pH 7.0–8.5, ammonia acts as a base in catalyzing the condensation of formaldehyde with bis(alaninato)copper(II) to give the expected copper(II) complex of 4-methyloxazolidine-4′-carboxylic acid [5–9].

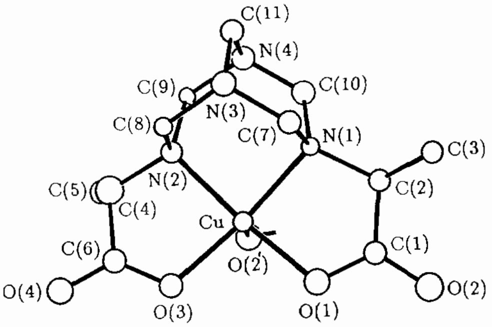

Fig. 1. Molecular structure and numbering scheme employed for $[Cu(C_{11}H_{18}N_4O_4)]_n$. Selected interatomic parameters: Cu–O(1) 1.95(2), Cu–O(3) 1.95(2), Cu–N(1) 2.05(2), Cu–N(2) 2.00(2), Cu–O(2′) 2.13(2) Å; O(1)–Cu–O(3) 96.5(7), O(1)–Cu–N(1) 84.8(7), O(3)–Cu–N(2) 85.8(7), N(1)–Cu–N(2) 87.7(7), O(1)–Cu–O(2′) 97.0(7), O(3)–Cu–O(2′) 95.7(7), N(1)–Cu–O(2′) 96.6(7), N(2)–Cu–O(2′) 106.9(7), and Cu–O(2′)–C(1′)°. The primed atoms are related by the symmetry operation: $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

However, in the present reaction the α-carbon atoms of Cu(L-ala)$_2$ are unaffected by formaldehyde attack as shown by the crystal structure in Fig. 1. Instead, formaldehyde condenses with ammonia, the pentamethylenediamine group so formed bridges the two chelated alanine ligands via both nitrogen atoms of the alanine moieties; the overall structure is akin to hexamine. The two alanine rings in the resultant complex are *cis* with respect to each other which implies that the initial *trans*-Cu(L-ala)$_2$ [10] must have undergone rearrangement to give the ligand configuration in the final product; Fig. 1. Only one other example of such *trans* → *cis* conversion in the configuration of ligands has been encountered [4] as thus far reactions of amino acid complexes with aldehydes have always resulted in the *trans* product irrespective of whether the starting ligands are *cis* or *trans* [5–9].

Preliminary studies [11] have shown that if the reaction is performed at pH 8.5–9.2 the same product is obtained. Under similar conditions Zn(L-ala)$_2$ also gives a similar product whereas Ni(ala)$_2$ yields hexamine in all cases.

In the complex the Cu atom is five coordinate and exists in a distorted square pyramidal environment as shown in Fig. 1. The basal plane is defined by two oxygen atoms and two nitrogen atoms derived from the alanine residues which are linked via the pentamethylenediamine group as described above. The Cu atom lies 0.364(4) Å out of the basal plane (deviations from least-squares plane: O(1) 0.09(2); O(3) −0.08(2); N(1) −0.09(2); N(2) 0.10(2) Å) in the direction of the C(5) atom. The axial position is occupied by a symmetry related O(2′) atom (symmetry operation: $-x, \frac{1}{2}+y, \frac{1}{2}-z$) so that an infinite polymeric chain is generated, in the *b* axis direction, as highlighted in Fig. 2.

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*Authors to whom correspondence should be addressed.

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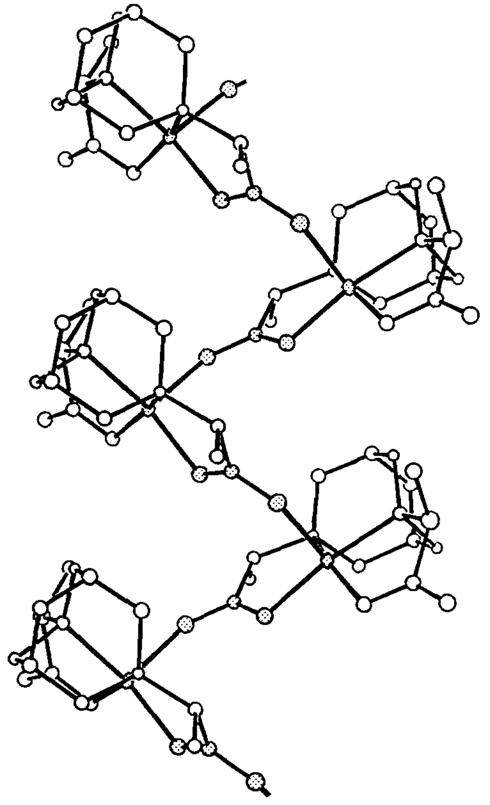

Fig. 2. Diagram showing the polymeric nature of $[Cu(C_{11}H_{18}N_4O_4)]_n$ in the solid state; the backbone of the polymer is highlighted by shading.

Experimental

A reaction mixture consisting of bis(L-alaninato)-copper(II) (1.9 g, 0.008 mol) and 15 cm^3 of a 40% wt./vol. solution of formaldehyde (0.2 mol) was stirred thoroughly and its pH adjusted to 8.5 by the slow addition of concentrated ammonia solution. On standing for a week, blue needle-shaped crystals appeared. These were filtered, washed with ethanol and acetone and were finally dried *in vacuo* at 50 °C for 10 h; the crystals were examined subsequently by single-crystal X-ray analysis. *Anal.* Found: C, 39.5; H, 5.3; N, 16.9. Calc. for $C_{11}H_{18}CuN_4O_4$: C, 39.6; H, 5.4; N, 16.8%.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer fitted with Mo Kα radiation, λ = 0.7107 Å. Of the 1581 data measured (θ_{max} 25°), 1403 were unique and of these 744 absorption corrected data satisfied $I \geqslant 2.5\sigma(I)$.

Crystal data for $C_{11}H_{18}CuN_4O_4$: M_r = 338.8, orthorhombic, space group $P2_12_12_1$; a = 12.370(4), b = 6.358(3), c = 26.029(4) Å; U = 1260.7 Å^3, D_m = 1.73, Z = 4, D_c = 1.759 Mg m^{-3}; $F(000)$ = 692, μ = 17.21 cm^{-1}. The structure was solved by the Patterson technique and refined by a full-matrix least-squares procedure based on F [12]. The Cu atom was refined anisotropically and the remaining atoms were refined isotropically; hydrogen atoms were included in their calculated positions. At convergence final R = 0.075, R_w = 0.078 for $w = [\sigma^2(F) + 0.011F^2]^{-1}$ (for preferred chirality).

Supplementary Material

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters and structure factor amplitudes are available on request from author E.R.T.T.

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