

Reaction of Formaldehyde with Bis(glycinato)zinc(II): X-Ray Structure of Bis[*N*-(1,3-dioxo-5-azacyclohexyl)acetato]zinc(II) Dihydrate

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The novel zinc(II) complex formed by the reaction of formaldehyde with bis(glycinato)zinc(II) monohydrate in the absence of base has been shown by X-ray diffraction to be bis[*N*-(1,3-dioxo-5-azacyclohexyl)acetato]zinc(II) dihydrate.

Formaldehyde is known to undergo base-catalysed condensation reactions with bis(α -amino-acidato)metal(II) complexes with the formation of compounds containing oxazolidine-type rings,^{1–3} which, when treated under acid conditions, result in the isolation of the metal-free α -hydroxymethyl substituted amino-acid.^{4,5} However no such condensation reaction has been known to occur in the absence of base nor has such a reaction involving bis(glycinato)zinc(II) been reported.

We report here, the novel reaction of bis(glycinato)zinc(II) monohydrate with an excess of formaldehyde in the absence of base (pH of reaction mixture was adjusted to 4.5) which was carried out at room temperature and which after three days afforded colourless parallelepiped-shaped crystals (insoluble

in cold water). Analytical data showed the crystals to be consistent with the formulation $C_{10}H_{20}N_2O_{10}Zn$.

Crystal data: $C_{10}H_{20}N_2O_{10}Zn$, $M = 393.6$, orthorhombic, space group *Pbca*, $a = 17.537(4)$, $b = 11.596(4)$, $c = 7.310(5)$ Å, $U = 1486.6$ Å³, $Z = 4$, $D_c = 1.758$, $D_m = 1.742$ g cm⁻³, $F(000) = 818$, Mo- K_α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo-}K_\alpha) = 16.95$ cm⁻¹.[†]

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

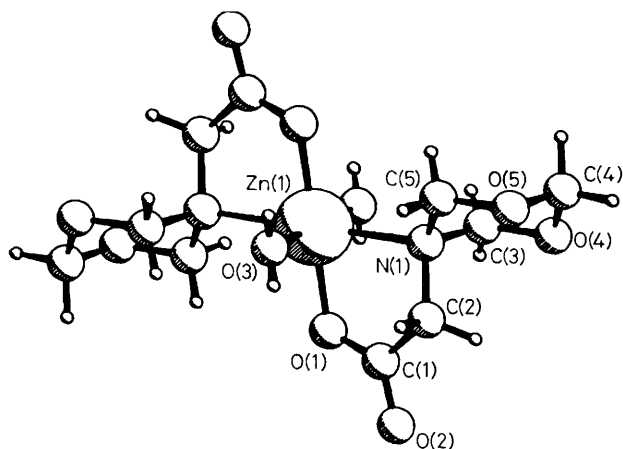


Figure 1. Molecular structure of $C_{10}H_{20}N_2O_{10}Zn$. Bond lengths: O(1)–Zn(1) 2.011(2), N(1)–Zn(1) 2.244(2), C(1)–O(2) 1.247(3), C(3)–N(1) 1.477(4), C(2)–C(1) 1.526(4), C(4)–O(4) 1.420(4), C(5)–O(5) 1.425(4), O(3)–Zn(1) 2.136(2), C(1)–O(1) 1.256(3), C(2)–N(1) 1.477(3), C(5)–N(1) 1.472(4), O(4)–C(3) 1.420(4), O(5)–C(4) 1.407(4) Å.

The intensities of 1665 reflections were measured on a STOE 2-circle Weissenberg diffractometer using Mo- K_α radiation and a graphite monochromator in the range $2.5 \leq 2\theta \leq 50^\circ$. Lorentz-polarization and absorption corrections were applied to these reflections. Of these, 1356 reflections with $I > 2.5\sigma(I)$ were considered observed. The maximum and minimum transmission factors were 0.7968 and 0.3360 respectively. The structure was solved by standard heavy atom methods and refined by full-matrix least-squares to a current conventional $R = 0.0416$ and a weighted $R = 0.0410$ based on counting statistics.

The molecular structure is shown in Figure 1. It comprises two five-membered rings resulting from the complexation of glycine on the zinc atom and two six-membered rings, basically of chair conformation, resulting from the condensation of formaldehyde molecules at the nitrogen atom. The six-membered ring resembles a substituted metaformaldehyde (trioxan) with one of the oxygen atoms of the metaformaldehyde being replaced by the nitrogen atom of glycine. The

hexaco-ordination for the zinc atom is completed by two water molecules and the amino- and carboxy groups.

The formation of the zinc(II) complex of *N*-(1,3-dioxo-5-azacyclohexyl)acetic acid must necessarily involve the loss of protons from the nitrogen atom of bis(glycinato)zinc(II), a phenomenon which has been extensively studied.^{1–3,4,6} This leads to the electrophilic attack on the nitrogen atom by formaldehyde molecules, followed by cyclization to give the six-membered *N*-substituted metaformaldehyde ring.

For the base-catalysed condensation reaction, the initial loss of nitrogen protons is accompanied by the dissociation of protons on the α -carbon atom^{1,2,4} and attack by formaldehyde molecules, but in the present reaction the α -carbon atom is *unaffected* by the formaldehyde attack.

Preliminary work⁷ has shown that formaldehyde undergoes the same type of condensation reaction with the bis(glycinato)-complexes of copper(II), nickel(II), and cobalt(II), the products of which yield glycine and formaldehyde when treated with H_2S .

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