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Condensation of Bis(glycinato)nickel(II) with Formaldehyde and Ammonia: X-ray Structure of Bis[3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)diacetato]-nickel(II)

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While the reactions of bis(α-aminoacidato)metal-(II) complexes with aldehydes have been extensively studied [1–5], the corresponding nickel(II) complexes have only received scant attention [6].

A recent study [7] has shown that, in the absence of base, the reaction of bis(glycinato)nickel(II) dihydrate, $Ni(gly)_2\cdot 2H_2O$, with formaldehyde results in the formation of an N-substituted metaformaldehyde ring arising from the condensation of formaldehyde molecules at the nitrogen atom of the glycine chelate. However, there is no report to date of the corresponding reaction in basic medium.

In this paper we report the reaction of bis(glycinato)nickel(II) dihydrate with formaldehyde and ammonia (pH of the reaction mixture was adjusted to 8.5) which was carried out at room temperature. After a week the reaction afforded (in 75% yield) orange needle-shaped crystals, which were insoluble in cold water and common organic solvents. Analytical data showed the crystals to be consistent with the formulation $C_9H_{14}N_4O_4Ni$.

Crystal Data: $C_9H_{14}N_4O_4Ni$, $M = 300.95$, orthorhombic, space group $Pna2_1$, $a = 10.647(2)$, $b = 14.716(3)$, $c = 6.751(10)$ Å, $U = 1057.7$ Å^3, $Z = 4$, $D_c = 1.890$, F(000) = 624, Mo-K_α radiation ($\lambda = 0.7107$), μ(Mo-K_α) = 18.5.

The intensities of 847 reflections were measured on a CAD-4 diffractometer using Mo-K_α radiation and a graphite monochromator in the range $1.5 < \theta < 25°$. Lorentz polarization and absorption corrections were applied to these reflections, of which 607 with $I > 2.5\sigma(I)$ were considered observed. The structure was solved by standard heavy atom methods and refined by a weighted full-matrix least-squares (including hydrogens at calculated positions) to an $R = 0.033$ and $R_w = 0.034$.

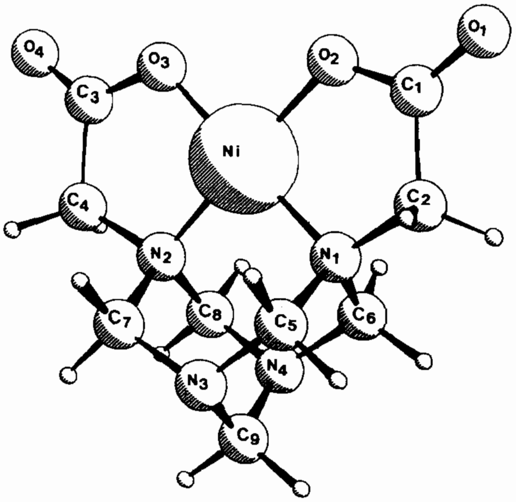

Fig. 1. Molecular structure of $C_9H_{14}N_4O_4Ni$. Bond lengths: Ni–N(1) 1.911(7), Ni–N(2) 1.907(7), Ni–O(2) 1.846(5), Ni–O(3) 1.842(5), C(1)–O(1) 1.221(10), C(1)–O(2) 1.304(10), C(1)–C(2) 1.506(13), C(3)–O(3) 1.308(11), C(3)–O(4) 1.192(10), C(3)–C(4) 1.521(12), N(1)–C(2) 1.502(13), N(2)–C(4) 1.508(10) Å; Angles: N(1)–Ni–N(2) 91.0(3), O(3)–Ni–N(2) 89.1(3), O(3)–Ni–O(2) 91.5(2), O(2)–Ni–N(1) 88.3(3)°.

The molecular structure is shown in Fig. 1. It shows that the two glycine rings have been bridged by a pentamethylene diamine grouping akin to the structure of hexamethylene tetramine (formed by formaldehyde-ammonia reaction under appropriate conditions [8]). The ligating atoms and nickel are closely coplanar and lie in a pseudo mirror plane of the space group (a true mirror in *Pnam*). The errors on the bridge atoms of this plane are large and the ten C–N bonds average 1.48(2) Å, and ranging from 1.41(4) to 1.62(4) Å. The errors in the glycinate fragments are small and clearly show that the complex is low-spin (*cf.* high-spin $Ni(gly)_2\cdot 2H_2O$ were Ni–N = 2.08(1), Ni–O = 2.06(1) Å [9]) which is supported by magnetic moment measurements showing that the complex is diamagnetic. Compared to the structure of $Ni(gly)_2\cdot 2H_2O$, the complex has little ring puckering, chelate ring angles near 90° (*cf.* 81.1(5)° in $Ni(gly)_2\cdot 2H_2O$) and a very large difference in the bond lengths within the carboxylate groups, 0.10(2) Å (*cf.* 0.02(2) Å in $Ni(gly)_2\cdot 2H_2O$).

It has been demonstrated that in the presence of a base the protons on the α-carbon atoms of coordinated amino acids are labile [10]. However, although the present reaction had been carried out in the presence of ammonia, the α-carbon atoms of $Ni(gly)_2\cdot 2H_2O$ have been found to be *unaffected* by formaldehyde attack, in contrast to the electrophilic attack of aldehydes on α-carbon atoms observed in base-catalyzed condensation reactions of α-aminoacidato metal complexes with aldehydes [1–6]. In some of the reactions currently being studied [11], ammonia has been found to catalyze formaldehyde

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attack on the α-carbon atoms of coordinated amino acids but in the present reaction it condenses with formaldehyde and Ni(gly)$_2$·2H$_2$O. This leads to the formation of the pentamethylene diamine bridge [12] and a structure having a flattened chair–chair conformation, which is favoured in various heterocyclic bicyclo[3.3.1]nonanes [13].

The two glycine rings in the resultant complex are *cis* with respect to each other, which implies that they must have undergone 'rearrangement' from the initial *trans*-Ni(gly)$_2$·2H$_2$O [9, 14]. In the reactions of α-aminoacidato metal complexes with the aldehydes studied so far we have encountered instances where the α-aminoacidato metal complex initially has a *cis* or *trans* structure but after condensation with an aldehyde the resultant metal-containing product possesses a *trans* configuration of ligands [1–7, 15]. However, there has been no precedence of the *trans* → *cis* conversion in the configuration of ligands as observed in the present reaction.

When the reaction of Ni(gly)$_2$·2H$_2$O with formaldehyde and ammonia was carried out at pH 7.5, fine green crystals were obtained. Early studies [11] seem to indicate that formaldehyde attacks both the nitrogen and α-carbon atoms of Ni(gly)$_2$·2H$_2$O to give an oxazolidine ring (infrared absorption spectrum of complex shows a triplet in the 1200–1080 cm^{-1} region characteristic of the oxazolidine system [16]). At pH values between 7.5 and 8.5 both the orange and green products have been obtained [17], whereas in other reactions of bis(α-aminoacidato)metal(II) complexes with aldehydes carried out in basic media, only one meta-containing product has been isolated in each instance [1–6].

Preliminary work [11] has shown that the bis(glycinato)- complexes of copper(II) and zinc(II) also undergo similar reactions with formaldehyde and ammonia.

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17 X-ray structure analysis of the green product has so far not been successful owing to difficulty in obtaining suitable crystals.