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Nature of the Metal(II) Complexes Formed in the Reactions of Formaldehyde with the Bis(glycinato) Complexes of Nickel(II), Cobalt(II) and Copper(II) at pH 4.5

SO'ON-BENG TEO and SIANG-GUAN TEOH

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

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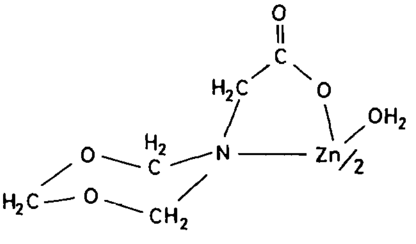
A recent investigation [1] has shown that, in the absence of base, the reaction of formaldehyde with bis(glycinato)zinc(II) monohydrate results in the formation of the complex, bis[N-(1,3-dioxa-5-azacyclohexyl)acetato]zinc(II) dihydrate, *1*.



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The molecular structure of *1* 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. Two water molecules attached to zinc complete the hexacoordination for the metal atom.

The present paper reports a study of the metal(II) complexes obtained from the reactions of formaldehyde with the bis(glycinato)- complexes of nickel(II), cobalt(II) and copper(II). The reactions, carried out in the absence of base (pH 4.5), gave light blue, pink and deep blue crystalline products respectively. The reaction products are all insoluble in cold water and in common organic solvents and when they are treated with H_2S, glycine is obtained in each instance.

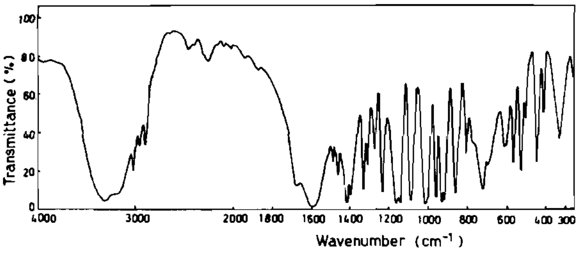

Fig. 1. Infra-red spectrum of M(II)DAA (M = Zn, Ni, Co).

The infra-red absorption spectra of both the nickel(II) and cobalt(II) products are identical with that of *1* (Fig. 1), which leads us to propose a similar structure for the respective nickel(II) and cobalt(II) complexes. The infrared spectrum of the copper(II) product also closely resembles that of *1*, apart from the absence of absorptions due to water in the frequency range 3600–3200 cm^{-1}; hence the copper(II) complex has been tentatively assigned a similar structure to that of *1*. In addition, microanalysis results (Table I) agree closely with their proposed molecular formulae. All the above complexes (henceforth abbreviated as M(II)DAA where M = Zn, Ni, Co, Cu) do not exhibit any characteristic absorption due to the $-NH_2$ or $\rangle NH$ groups (a fact which further supports their proposed structures) but show typical carboxylate asymmetric and symmetric stretching frequencies at ~1630–1580 cm^{-1} and ~1430–1390 cm^{-1} respectively.

The molecular formula of each of the M(II)DAA complexes (M = Ni, Co) suggests that there are two molecules of water, the presence of which is indicated by a broad band centred at ~3300 cm^{-1} in the infra-red spectrum of the complex. As these water molecules are not easily removed (thermal analysis results [2] show that Ni(II)DAA and Co(II)-

TABLE I. Microanalysis Results of M(II)DAA.

M(II)DAA	Formula	Calculated				Found			
		%C	%H	%N	%M	%C	%H	%N	%M
Ni(II)	$C_{10}H_{20}N_2O_{10}Ni$	31.0(4)	5.2(1)	7.2(4)	15.2	30.6	5.3	7.4	15.3
Co(II)	$C_{10}H_{20}N_2O_{10}Co$	31.0(2)	5.2(1)	7.2(3)	15.2(1)	30.6	5.4	6.9	15.4
Cu(II)	$C_{10}H_{16}N_2O_8Cu$	33.8	4.5	7.8	17.9	33.6	4.5	7.6	17.8

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TABLE II. Interplanar Spacings (d-Values in Angstroms) for M(II)DAA (M = Zn, Ni, Co). The eight most intense lines are listed.

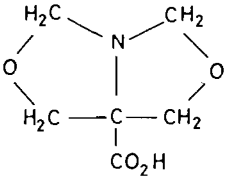
M = Zn	M = Ni	M = Co
8.9s[a]	8.9s	8.9s
5.8s	5.9s	5.8s
5.0w	4.9w	4.9w
4.5m	4.4m	4.5m
4.0m	3.9m	3.9m
3.5w	3.4w	3.4w
2.6m	2.5m	2.5m
2.2m	2.1m	2.2m

[a] s = strong, m = medium, w = weak.

DAA both decompose exothermically at 255 °C and their respective thermograms do not indicate any weight loss due to water molecules alone) it is assumed that they exist as structural water.

An examination of the X-ray powder diagrams of Ni(II)DAA and Co(II)DAA reveals that their general line patterns are almost identical with that observed for Zn(II)DAA (Table II). It is therefore likely that the metal ions in the nickel(II) and cobalt(II) complexes are also octahedrally coordinated as in the case of the zinc(II) complex. Furthermore, the room-temperature magnetic moments of these complexes as well as their electronic spectra (Table III) are consistent with those found for complexes having octahedral geometry [3]. The value of the room-temperature magnetic moment (1.90 B.M.) and the electronic spectrum (broad band at 17,200 cm^{-1}) for Cu(II)DAA both lie in the range for tetragonally octahedral copper(II) complexes [4] but the nature of the hexacoordination of the copper(II) ion is unclear to us at the moment.

Recently [5], we carried out the base-catalyzed reaction of formaldehyde with bis(glycinato)copper(II) which resulted in the formation of the copper(II) complex of *2*. In this reaction, the initial loss of



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protons from the nitrogen and α-carbon atoms of the coordinated glycine is followed by formaldehyde attack to form hydroxymethyl species and subsequent cyclization occurs to give oxazolidine rings. In the present work, however, the α-carbon atoms of the bis(glycinato)metal(II) complexes have been shown to be unaffected by formaldehyde attack. Instead, after the initial loss of protons from the nitrogen atom of the coordinated glycine, electrophilic attack by formaldehyde molecules takes place at the nitrogen atom, giving rise to a bis-hydroxymethyl species. Further addition of a molecule of formaldehyde then occurs to given an N-substituted metaformaldehyde species.

Experimental

Reagents

The bis(glycinato)metal(II) complexes were prepared according to previously reported procedures [6].

Reagent grade chemicals were used in all the reactions.

Preparation of Compounds

All the M(II)DAA complexes were prepared according to the method described as follows.

TABLE III. Magnetic Moments and Electronic Spectra of M(II)DAA.

M(II)DAA	Magnetic Moment (B.M.)	Band in Electronic Spectrum (cm^{-1})	Tentative Assignment of Transition
Ni	3.18	27,000	$^3T_{1g} \leftarrow {}^3A_{2g}$
		15,900[b]	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$
Co	4.85	21,000[c]	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$
Cu	1.90	17,200	d

[b] The expected $^3T_{2g} \leftarrow {}^3A_{2g}$ transition for an octahedral nickel(II) complex which occurs at a much lower frequency could not be detected. [c] The $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ transition which is expected for an octahedral cobalt(II) complex is very 'weak' and that combined with its closeness to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ band resulted in the transition being unobserved. The $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ transition which is expected to occur at a much lower frequency could not be detected in the frequency range determined. [d] See Ref. 4.

A reaction mixture consisting of the appropriate bis(glycinato)metal(II) complex (0.01 mol) and formaldehyde (30 cm^3 of a 40% w/v solution) was stirred thoroughly and its pH was adjusted to 4.5 by dilution with distilled water. The reaction mixture was then filtered and the filtrate was allowed to stand for three days at room temperature.

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

Physical Measurements

All microanalyses were carried out by the Australian Microanalytical Service, Australian Mineral Development Authorities, Port Melbourne, Australia. The results are shown in Table I.

Infra-red absorption spectra of the compounds were recorded using a Beckman IR 20A infra-red spectrophotometer. Samples were prepared as KBr discs.

X-ray powder diagrams were obtained with a Phillips PW 1380 diffractometer using Cu-K$_\alpha$ radiation. Interplanar spacings calculated from the eight most intense lines are listed in Table II.

The magnetic moments of the complexes were determined by the Gouy method [7, 8]. The magnetic field, calibrated with Hg[Co(CNS)$_4$] (χ_g = 16.44 × 10^{-6} c.g.s. at 20 °C) was produced by a Newport Type A electromagnet (with shimmed pole tips coned to 75 mm diameter and special magnetic shunt). Diamagnetic corrections were estimated from Pascal's constants [7].

The electronic spectra (in the frequency range 40,000–11,000 cm^{-1}) of the compounds (Table III) were obtained by means of a Hitachi 200-10 spectrophotometer using the nujol mull technique.

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