Inorganica Chimica Acta, 70 (1983) 107–110

The Preparation and Characterization of some Metal(II) Complexes of Dihydro-1H,3H,5H-oxazolo[3,4-c] oxazole-7a-carboxylic Acid

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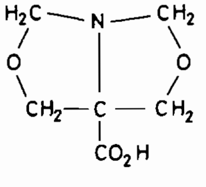
Received July 2, 1982

The metal(II) (metal = copper, nickel, cobalt and zinc) complexes of dihydro-1H,3H,5H-oxazolo-[3,4-c] oxazole-7a-carboxylic acid have been prepared by various reaction pathways and characterized by microanalysis and magnetic moment measurements, as well as examinations of electronic and infrared spectra.

Introduction

The reactions of α-aminoacidato metal complexes with aldehydes have been extensively studied [1–12] but in many instances the metal-containing products have not been isolated.

A recent investigation [1] has shown that the base catalyzed reaction of bis(L-serinato)copper(II) with formaldehyde results in the formation of the bis(aminoacidato)copper(II) complex of dihydro-1H, 3H,5H-oxazolo[3,4-c] oxazole-7a-carboxylic acid, *1*[*].



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The present paper gives details of the preparation of the bis(chelate)metal(II) complexes of *1* (metal = copper, nickel, zinc and cobalt) by several reaction pathways. The complexes are then characterized by microanalysis and magnetic moment measurements, as well as by examinations of electronic and infrared spectra.

Experimental

Reagents

L-serine was used as supplied by B.D.H. Chemical Company. α-Hydroxymethylserine was prepared according to the method of Christensen [13], and also by a recently reported method [14].

Formaldehyde was obtained as a 40% w/v aqueous solution from May & Baker Pty. Ltd.

The bis(L-serinato)metal(II) complexes [M(L-ser)$_2$, M = Cu, Ni, Zn] were prepared by previously described methods [12, 15–17], while the bis(α-hydroxymethylserinato)metal(II) complexes were obtained as reported by Brush [12].

Preparation of Compounds

Cu(II)DO$_2$CA

The compound was prepared by the following methods:

(i) *The reaction of bis(glycinato)copper(II) with formaldehyde and base*

This method of preparing Cu(II)DO$_2$CA has been described previously [9].

(ii) *The reaction of bis(L-serinato)copper(II) with formaldehyde and base*

The preparation of Cu(II)DO$_2$CA by this method has been reported previously [1, 14].

(iii) *The reaction of bis(L-serinato)copper(II) with formaldehyde (without base)*

A reaction mixture consisting of bis(L-serinato)-copper(II) (1.3 g, 0.05 mol) and formaldehyde (10

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[*] The metal(II) complexes of *1* are abbreviated as M(II)-DO$_2$CA (M = Cu, Ni, Zn, Co).

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TABLE I. Microanalysis Results and Magnetic Moments of M(II)DO$_2$CA.

M(II)DO$_2$CA	Formula	Calculated			Found			Magnetic Moment (B.M.)
		C(%)	H(%)	N(%)	C(%)	H(%)	N(%)	
Cu(II)	$C_{12}H_{16}N_2O_8Cu$	37.95	4.24	7.37	37.96	4.25	7.10	1.93 ± 0.02
Ni(II)	$C_{12}H_{20}N_2O_{10}Ni$	35.06	4.90	6.83	35.31	4.88	7.01	3.38 ± 0.02
Zn(II)	$C_{12}H_{16}N_2O_8Zn$	37.77	4.26	7.34	37.76	4.43	7.37	Diamagnetic
Co(II)	$C_{12}H_{18}N_2O_9Co$	36.65	4.61	7.12	36.80	4.38	7.24	4.97 ± 0.01

cm^3) was diluted to 30 cm^3 with distilled water and refluxed at 120 °C for 12 h.

The deep blue crystals which resulted on cooling were filtered, washed successively with distilled water, ethanol and diethyl ether, and were finally dried under vacuum at 50 °C for 5 h. Yield 1.2 g (72%).

(iv) The reaction of bis(α-hydroxymethylserinato)-copper(II) with formaldehyde

A saturated aqueous solution containing bis(α-hydroxymethylserinato)copper(II) (2.0 g, 0.01 mol) was treated with formaldehyde (4 cm^3). After being stirred for 30 min the reaction mixture was allowed to stand overnight. The deep blue crystals which resulted were treated as before. Yield 1.9 g (83%).

(v) *The reaction of copper(II) acetate with α-hydroxymethylserine, formaldehyde and base*

An aqueous solution containing α-hydroxymethylserine (2.7 g, 0.02 mol), formaldehyde (3 cm^3) and potassium hydroxide (1.1 g, 0.02 mol) was treated with copper(II) acetate monohydrate (2.9 g, 0.02 mol) and the reaction mixture was warmed to 50 °C. After the copper(II) oxide which was initially formed was filtered, the dark green filtrate was allowed to stand for a week whence large blue crystals were formed. These were treated as before. Yield 1.4 g (36%).

M(II)DO$_2$CA (M = Ni, Zn, Co)

The nickel and zinc compounds were prepared according to methods (ii), (iv) and (v) while the cobalt compound was prepared by methods (iv) and (v) as described for the preparation of the copper compound.

Characterization of Compounds

Microanalysis

All microanalyses were carried out by the Australian Microanalytical Service, Division of Chemistry, C.S.I.R.O. and University of Melbourne. The results are shown in Table I.

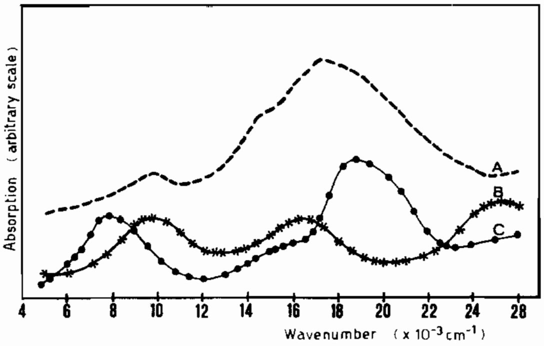

Fig. 1. Solid Reflectance Spectra of Cu(II)DO$_2$CA (A), Ni(II)DO$_2$CA (B) and Co(II)DO$_2$CA (C).

Magnetic Moment Measurement

The magnetic moments of the compounds were determined by the Guoy method [18, 19]. The magnetic field, calibrated with Hg[Co(CNS)$_4$] (χ_g = 16.44 × 10^{-6} c.g.s. at 20 °C), was produced by means of a Varian Associates Model V4005 four-inch electromagnet.

Diamagnetic corrections were estimated from Pascal's constants [18].

All measurements were done in duplicate and the results are given in Table I.

Electronic Spectral Analysis

The diffuse reflectance spectra of M(II)DO$_2$CA (M = Cu, Ni Co) (Fig. 1) were recorded on a Carl-Zeiss PMQII spectrophotometer. Analar magnesium oxide was the calibrant used.

Infrared Spectral Analysis

All the infrared spectra (Fig. 2) were recorded (in the frequency range 4000–250 cm^{-1}) using a Perkin Elmer 457 Infrared Absorption Spectrophotometer and were calibrated with air and polyotyrene.

The samples were prepared as potassium bromide discs.

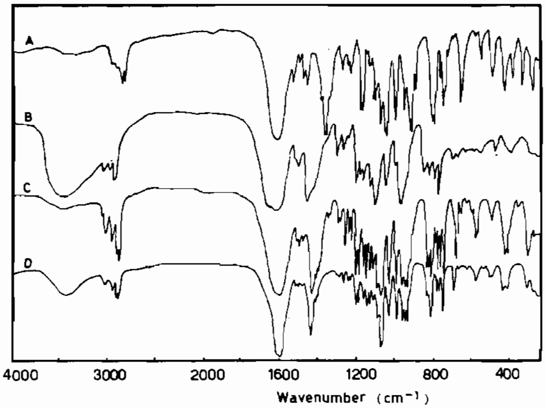

Fig. 2. Infrared Spectra of Cu(II)DO$_2$CA (A), Ni(II)DO$_2$CA (B), Zn(II)DO$_2$CA (C) and Co(II)DO$_2$CA (D).

Results and Discussion

Magnetic Moment and Electronic Spectral Analysis

Cu(II)DO$_2$CA

X-ray structure analysis [1] has shown that the metal(II) ion in Cu(II)DO$_2$CA is five coordinate. The room temperature magnetic moment of the compound (Table I) is normal for high-spin copper(II) complexes [18, 20, 21] and is consistent with the copper(II) ion being in an orbitally non-degenerate state of the type $^2B_1$ or $^2A_1$ [20, 22].

The electronic spectrum of the compound (Fig. 1) which closely resembles that of the square pyramidal complex [Cuen$_2$NH$_3$][BF$_4$]$_2$ [22] exhibits a broad band at approximately 17,400 cm^{-1} with a shoulder on the low frequency side. In the C_{4v} (square pyramidal) symmetry (which may be considered to result from distortions in the D_{4h} or O_h symmetries), three bands are expected. The observed band at 17,400 cm^{-1} and its shoulder on the low frequency side are tentatively assigned to the $^2E \leftarrow {}^2B_1$ and $^2B_2 \leftarrow {}^2B_1$ transitions respectively while the small band at approximately 10,000 cm^{-1} may be ascribed to the $^2A_1 \leftarrow {}^2B_1$ transition.

Ni(II)DO$_2$CA

The empirical formula of the complex suggests that there are two molecules of water, the presence of which is evidenced by the absorption at 3700–3300 cm^{-1} in the infrared spectrum (Fig. 2). As thermal analysis [23] has shown that these water molecules are not easily removed, it is appropriate to assume that they are structural water which coordinate to the nickel ion, resulting in an octahedral arrangement about the metal ion.

The magnetic moment of the complex (Table I) lies at the top of the range of values found for octahedral nickel(II) complexes but Lever [24] has shown that tetragonally distorted nickel(II) complexes can have moments as high as 3.50 B.M.

The electronic spectrum of Ni(II)DO$_2$CA which exhibits three bands at 25,600 cm^{-1}, 18,600 cm^{-1} and 9,600 cm^{-1} respectively is similar to those of many other octahedral nickel(II) complexes [21, 24–26]. According to Ligand Field Theory, three bands are associated with the spin allowed transitions of the $^3A_{2g}$ ground term of the nickel(II) ion. Hence, by comparison with the electronic spectra of other octahedral nickel(II) complexes, the bands at 25,600 cm^{-1}, 16,800 cm^{-1} and 9,600 cm^{-1} are tentatively assigned to $^3T_{1g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{2g} \leftarrow {}^3A_{2g}$ transitions respectively.

Co(II)DO$_2$CA

Microanalysis results suggest that the cobalt(II) complex possesses one molecule of water which is confirmed by the infrared absorption at 3650–3310 cm^{-1}. That the water molecule is coordinated to the cobalt(II) ion has been confirmed by thermal analysis results [23] which show that the cobalt(II) complex undergoes an exothermic decomposition reaction in the temperature range 320–383 °C and the thermogravimetric curve does not indicate any weight loss due to the elimination of a water molecule alone.

The magnetic moment of the complex indicative of an octahedral cobalt(II) configuration [18, 20, 21, 27–32] (tetrahedral cobalt(II) complexes normally have moments of 4.1–4.7 B.M. [18, 20, 21, 28] while square planar and five-coordinate cobalt(II) usually have much lower moments [21, 33, 34]).

The solid reflectance spectrum of compound shows two principal regions of absorption which is typical of six-coordinate cobalt(II) complexes [35–37]. The band at 18,800 cm^{-1} may be assigned to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition while that at 7,800 cm^{-1} may be assigned to the $^4T_{2g} \leftarrow {}^4T_{1g}(F)$ transition. The shoulder at around 16,300 cm^{-1} is tentatively assigned to the $^4A_{2g} \leftarrow {}^4T_{1g}(F)$ transition which, owing to its 'weakness' and its closeness to the $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ band, is sometimes not observed [21, 35].

In the cobalt(II) complex, it is possible that a water molecule coordinates to the metal ion while the sixth coordination is provided by a Co-O (from the carboxyl group of a neighbouring molecule) interaction [1].

Infrared Analysis

The infrared spectrum of Zn(II)DO$_2$CA (Fig. 2) closely resembles that of the copper(II) complex; hence it is tentatively assigned the same structure as that of Cu(II)DO$_2$CA.

Apart from the absorption bands due to structural water, the spectra of the nickel(II) and cobalt(II) complexes are also appreciably similar to those of the copper(II) and zinc(II) complexes.

All the M(II)CO_2CA complexes do not exhibit any characteristic absorption due to the $-NH_2$ or $=NH$ groups (which further support their proposed structures) but show typical carboxylate asymmetric and symmetric stretching frequencies at ~1635–1592 cm^{-1} and ~1433–1385 cm^{-1}, respectively.

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