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The Preparation and X-ray Crystal Structures of Bis(4R-oxazolidine-4′-carboxylato)copper(II) (R = Methyl, Phenyl)

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Abstract

The base-catalyzed condensation reactions of formaldehyde with the copper(II) chelates of α-alanine and C-phenylglycine result in the formation of bis(4R-oxazolidine-4′-carboxylato)copper(II) where R = methyl and phenyl respectively. The 4-methyl complex, $C_{10}H_{20}N_2O_8Cu$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.141(2)$, $b = 7.335(3)$, $c = 11.112(3)$ Å, $\beta = 103.87(2)°$ and $Z = 2$. The structure has been refined to $R = 0.026$ and $R_w = 0.031$ based on 749 independent reflections collected, 651 used. The geometry about copper is essentially a (4 + 2)-elongated octahedral structure. The 4-phenyl derivative, $C_{20}H_{20}N_2O_6Cu$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.939(4)$, $b = 8.887(2)$, $c = 8.611(3)$ Å, $\beta = 95.61(3)°$ and $Z = 2$. Refinement of the structure converged to $R = 0.062$ and $R_w = 0.071$ based on 1003 reflections collected and 865 used. The structure of the 4-phenyl complex resembles that of the 4-methyl derivative and differs mainly from the latter in being anhydrous.

Introduction

In recent years, extensive studies had been carried out on the reactions of formaldehyde with α-aminoacidato metal complexes [1–6]. However, such reactions involving coordinated α-alanine and C-phenylglycine have not been investigated.

In view of the above, we carried out the reactions of formaldehyde with the copper(II) chelates of the above two amino acids, which resulted in the formation of bis(4R-oxazolidine-4′-carboxylato)copper(II) where R = methyl and phenyl respectively. The preparation and X-ray crystal structures of the title compounds are reported herein.

Experimental

1. *Preparation of Compounds*

(a) Bis(4-methyloxazolidine-4′-carboxylato)-copper(II), $C_{10}H_{20}N_2O_6Cu$

Bis(α-alaninato)copper(II) was prepared as previously described [7]. To a 30 cm^3 aqueous solution of bis(α-alaninato)copper(II) (2.4 g, 0.01 mol) was added 30 cm^3 of a 40% w/v solution of formaldehyde (0.4 mol). The pH of the mixture was adjusted to 8.0 by the addition of concentrated ammonia solution. The reaction mixture was then allowed to stand for a week at room temperature whence deep blue crystals appeared. These were filtered, washed successively with cold distilled water, ethanol and acetone and were finally dried under vacuum for 5 h. Yield 2.5 g (69%). *Anal.* Found: C, 33.2; H, 5.7; N, 7.8. Calcd. for $C_{10}H_{20}N_2O_8Cu$; C, 33.4; H, 5.6; N, 7.8%.

(b) Bis(4-phenyloxazolidine-4-carboxylato)copper-(II), $C_{20}H_{20}N_2O_6Cu$

A mixture containing C-phenylglycine (3.0 g, 0.02 mol) and sodium hydroxide (0.8 g, 0.02 mol) in 30 cm^3 distilled water was stirred thoroughly and then added to a saturated solution of copper(II) sulphate pentahydrate (2.5 g, 0.01 mol). The addition of 30 cm^3 of a 40% w/v formaldehyde solution (0.4 mol) followed and the pH of the reaction mixture was adjusted to 8.0 with concentrated ammonia solution. After filtration, the mixture was allowed to stand for 5 days after which deep blue crystals appeared. These were treated as for the 4-methyl derivative. Yield 3 g (67%). *Anal.* Found: C, 53.9; H, 4.8; N, 6.2. Calcd. for $C_{20}H_{20}N_2O_6Cu$: C, 53.6; H, 4.5; N, 6.2(5)%.

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TABLE I. Summary of Crystal Data and Experimental Details of the Structural Study of the 4-Methyl and 4-Phenyl Complexes.

	4-Methyl Complex	4-Phenyl Complex
Crystal system	Monoclinic	Monoclinic
a (Å)	9.141(2)	11.939(4)
b (Å)	7.335(3)	8.887(2)
c (Å)	11.112(3)	8.611(3)
β (°)	103.87(2)	95.61(3)
U (Å^3)	723.3	909.3
Space group	$P2_1/n$	$P2_1/c$
Z	2	2
D_c (g cm^{-3})	1.505	1.636
$F(000)$	342	462
Crystal dimensions (mm)	0.06 × 0.33 × 0.08	0.45 × 0.40 × 0.10
Radiation	Mo-K$_\alpha$ (λ = 0.7107 Å)	Mo-K$_\alpha$ (λ = 0.7107 Å)
Monochromator	Graphite	Graphite
Standards	3 reflections every hour	3 reflections every hour
No. of reflections collected	749	1003
No. of reflections with $I > 2.5\sigma(I)$	651	865
Absorption coefficient, μ (cm^{-1})	15.04	12.4
R	0.026	0.062
R_w	0.031	0.071

2. *Determination of X-ray Crystal Structures*

(a) X-ray Crystal Structure of $C_{10}H_{20}N_2O_8Cu$

(i) Collection of Intensity Data. A blue needle-shaped crystal was mounted on a glass fibre with epoxy resin. Precession photography was employed for preliminary analysis of crystal quality and indicated the monoclinic space group $P2_1/n$. Lattice parameters at 23 °C were determined by least squares fit to the setting of 25 independent reflections ($\theta < 20°$) measured and refined by scans performed on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite monochromated Mo-K$_\alpha$ radiation.

Intensity data were collected in the range $1.2 < \theta < 22°$ using an ω–$(n/3)\theta$ scan, where n (=2) was optimized by $\omega/2\theta$ profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures employed were $(1.0 + 0.35 \tan\theta)°$ and $(2.40 + 0.5 \tan\theta)$ mm respectively. The monitoring of standard reflections indicated that no decomposition occurred. The crystal data and experimental conditions employed for the structure determination are summarized in Table I.

(ii) Reduction of Intensity Data and Structure Solution and Refinement. Data reduction and application of Lorentz and polarization corrections Of the 749 independent reflections collected, 651 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

From the unit cell size, a Z of 2 was suggested. Consequently the copper was placed at a centre of symmetry and calculation of a difference Fourier revealed all non-hydrogen atoms. Anisotropic refinement of all the heavier atoms enabled the location of all hydrogen atoms which were also included and refined.

Full-matrix least-squares techniques were used for the refinement of all positional and thermal parameters and an overall scale factor. Refinement converged with $R(=\Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$ and R_w $(=\Sigma(|F_o| - |F_c|)w^{1/2}/-\Sigma(|F_o|w^{1/2}))$ values of 0.026 and 0.031 respectively with a weighting scheme of the form $w = 0.21/(\sigma^2 F_o + 0.0037{F_o}^2)$. A final difference map was structurally featureless with the largest peak being 0.25 e Å^{-3} in height. Final positional parameters for the heavier atoms are listed in Table II.

(iii) Brief Description of Structure and Discussion. A perspective view of the cation is shown in Fig. 1. The structure establishes the expected condensation of the aldehyde and amino acid moieties and the formation of a bidentate ligand. The centrosymmetric coordination suggests that racemization (probably at C(2)) has occurred on condensation. All bond lengths within the ligands are within the range observed in similar complexes [1, 9]. The geometry about copper is essentially a (4 + 2)-elongated octahedral structure. The Cu–N(1) and Cu–O(1) bond lengths are again typical [1, 9, 10] while

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*Computer programmes used are listed in ref. 8.

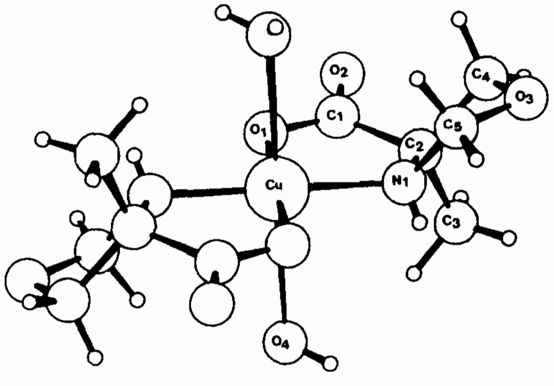

Fig. 1. Molecular structure of $C_{10}H_{20}N_2O_8Cu$.

TABLE II. Final Positional (×10^4) Parameters for $C_{20}H_{20}$-N_2O_8Cu.

Atom	x	y	z
Cu	0	0.5	0.5
O(1)	−264(3)	2960(3)	6051(2)
O(2)	−1864(3)	772(4)	6263(2)
O(3)	−4536(3)	4250(4)	3545(3)
O(4)	1274(4)	3013(5)	3625(4)
N(1)	−1946(3)	4172(4)	3913(4)
C(1)	−1452(4)	2023(5)	5662(4)
C(2)	−2419(4)	2425(5)	4374(3)
C(3)	−2291(6)	850(6)	3515(5)
C(4)	−4063(5)	2805(7)	4413(6)
C(5)	−3257(5)	5385(6)	3751(6)

TABLE III. Bond Distances (Å) And Valence Angles (°) for $C_{10}H_{20}N_2O_8Cu$.

O(1)–Cu	1.949(2)
N(1)–Cu	1.991(3)
C(1)–O(2)	1.245(4)
C(5)–O(3)	1.409(5)
C(5)–N(1)	1.468(5)
C(3)–C(2)	1.520(6)
O(4)–Cu	2.582(3)
C(1)–O(1)	1.270(4)
C(4)–O(3)	1.428(5)
C(2)–N(1)	1.482(5)
C(2)–C(1)	1.520(5)
C(4)–C(2)	1.540(6)
O(4)–Cu–O(1)	93.4(1)
N(1)–Cu–O(4)	86.2(1)
C(5)–O(3)–C(4)	102.9(3)
C(5)–N(1)–Cu	118.3(3)
O(2)–C(1)–O(1)	124.0(3)
C(2)–C(1)–O(2)	117.8(3)
C(3)–C(2)–N(1)	111.6(3)
C(4)–C(2)–N(1)	102.7(3)
C(4)–C(2)–C(3)	112.2(4)
N(1)–C(5)–O(3)	106.4(3)
N(1)–Cu–O(1)	84.7(1)
C(1)–O(1)–Cu	115.5(2)
C(2)–N(1)–Cu	110.3(2)
C(5)–N(1)–C(2)	105.7(3)
C(2)–C(1)–O(1)	118.2(3)
C(1)–C(2)–N(1)	109.9(3)
C(3)–C(2)–C(1)	109.2(3)
C(4)–C(2)–C(1)	111.1(3)
C(2)–C(4)–O(3)	104.8(3)

TABLE IV. Close Intermolecular Contacts (Å) for $C_{10}H_{20}$-N_2O_8Cu.

X–H–B	B–X	B–H
O(4)–H(1)–O(1)[a]	2.96	2.19
O(4)–H(2)–O(2)[b]	2.82	2.13
N(1)–H(3)–O(2)[a]	2.96	2.32

[a]Unit cell transformation: x, ½ − y, ½ + z. [b]Unit cell transformation: −x, −y, 1 − z.

were performed using programme SUSCAD* while absorption corrections were applied using ABSORB*. the long copper to water distance (2.582(3) Å) has been observed in a range of similar complexes [11]; for example in [Cu(L-histidinato)(D-histidinato)$(H_2O)_2]^{3+}$ the Cu–OH_2 separation is 2.57 Å [12]. Intramolecular distances and angles are listed in Table III.

Close intermolecular contacts which correspond to probable hydrogen bonds are listed in Table IV. Both water protons are involved in interactions as is the amine proton.

(b) X-ray Crystal Structure of $C_{20}H_{20}N_2O_6Cu$

(i) Collection of Intensity Data. A crystal shaped like an arrow head was mounted on a glass fibre with cyano–acrylate super glue. Lattice parameters at 25 °C were determined as for the 4-methyl compound.

Intensity data were collected in the range $1.5 < \theta < 24.5°$ using an ω–$(n/3)\theta$ scan where n (=3) was optimized by profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures were $(0.9 + 0.35 \tan \theta)°$ and $(2.40 + 0.5 \tan \theta)$ mm respectively. Again, the monitoring of standard reflections indicated that at the end of data collection, no decomposition had occurred. The crystal data and experimental conditions employed for the structure determination are shown in Table I.

(ii) Reduction of Intensity Data and Structure Solution and Refinement. The data were reduced and corrected in a manner similar to that for the 4-methyl derivative. The maximum and minimum transmission factors were estimated to be 0.94 and 0.84 respectively.

The structure was solved and refined by application of the heavy atom technique. Successive difference syntheses located all non-hydrogen atoms of the structure. In the refinement by full-matrix least-squares, the hydrogen atoms were allowed to ride in fixed orientation to their connections (NH and CH sites, d = 0.95 Å; (CH sites, d = 0.90 Å). A weighting scheme was applied and refined, converging at $w = 8.40/(\sigma^2 F_o + 0.0017 F_o^2)$. Refinement converged with R = 0.062 and R_w = 0.071 at which stage the largest peak in the final difference map was less than 0.9 e Å^{-3}. All scattering factors and anomalous terms were taken from International Tables [13]. The final positional parameters for the non-hydrogen atoms are listed in Table V while Table VI contains selected bond lengths and angles.

TABLE V. Final Positional (×10^4) Parameters for $C_{20}H_{20}N_2O_6Cu$.

Atom	x	y	z
Cu	0000(0)	0000(0)	0000(0)
N(1)	1614(6)	5185(7)	4082(7)
O(1)	−357(4)	6020(6)	3133(6)
O(2)	399(5)	7227(7)	989(7)
O(3)	−2626(6)	8565(7)	2668(7)
C(1)	2567(7)	7016(9)	2166(9)
C(2)	3631(9)	6677(11)	1506(13)
C(3)	4481(8)	7771(13)	1252(13)
C(4)	4228(11)	9221(14)	1716(13)
C(5)	3189(11)	9619(11)	2396(11)
C(6)	2359(7)	8496(10)	2640(9)
C(7)	447(7)	6444(9)	2158(9)
C(8)	1643(7)	5832(9)	2459(9)
C(9)	1866(8)	4402(10)	1496(11)
C(10)	2223(9)	3734(11)	3959(11)

TABLE VI. Selected Bond Lengths (Å) and Angles (°) for $C_{20}H_{20}N_2O_6Cu$.

Cu–N(1)	2.173(5)
C(8)–N(1)	1.511(10)
C(7)–O(1)	1.385(10)
C(2)–C(1)	1.469(14)
C(8)–C(1)	1.559(12)
C(4)–C(3)	1.388(17)
C(6)–C(5)	1.433(14)
C(9)–C(8)	1.551(12)
Cu–O(1)	1.855(5)
C(10)–N(1)	1.486(11)
C(7)–O(2)	1.218(9)
C(6)–C(1)	1.404(12)
C(3)–C(2)	1.435(14)
C(5)–C(4)	1.462(18)
C(8)–C(7)	1.523(11)
N(1)–Cu–O(1)	77.6(8)
C(10)–N(1)–C(8)	102.0(6)
C(8)–C(1)–C(2)	125.0(7)
C(3)–C(2)–C(1)	124.7(9)
C(5)–C(4)–C(3)	123.7(9)
C(5)–C(6)–C(1)	117.6(9)
C(8)–C(7)–O(1)	119.5(6)
C(1)–C(8)–N(1)	119.0(6)
C(7)–C(8)–C(1)	113.4(6)
C(9)–C(8)–C(1)	107.7(7)
N(1)–Cu–O(1)′	102.4(8)
C(6)–C(1)–C(2)	119.1(8)
C(8)–C(1)–C(6)	115.8(8)
C(4)–C(3)–C(2)	114.0(10)
C(6)–C(5)–C(4)	120.9(9)
O(2)–C(7)–O(1)	132.3(7)
C(8)–C(7)–O(2)	108.1(8)
C(7)–C(8)–N(1)	100.7(7)
C(9)–C(8)–N(1)	101.7(6)
C(9)–C(8)–C(7)	114.0(6)

(iii) Brief Description of Structure and Discussion.

A perspective view of the cation is shown in Fig. 2. The structure of this blue product is the one now generally expected for condensations of formaldehyde on α-carbon substituted amino acid com-

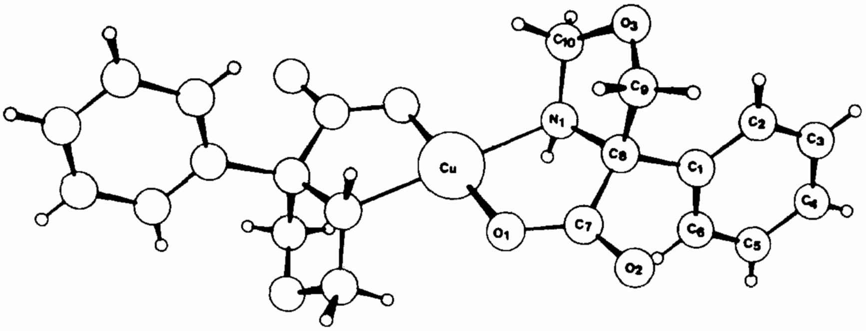

Fig. 2. Molecular structure of $C_{20}H_{20}N_2O_6Cu$.

plexes of copper(II), namely the formation of an oxazolidine ring fused across the nitrogen and α-carbon atoms. The 4-phenyl structure resembles the 4-methyl derivative and differs mainly from the latter in being anhydrous. While the copper square plane in the 4-methyl complex is completed by apical bonds to two water molecules, in the 4-phenyl structure, the square plane is completed by two very long bonds (2.63 Å) to O(2), the free carboxyl oxygen. The latter structure is not as accurate as the former one; the bond lengths and angles are similar but the C(7) to O(1) distance of 1.385 Å is at least 0.1 Å too long. The geometry of the methyl complex is very similar to that of bis(glycinato)copper(II) itself [10] to within several standard deviations. However, the phenyl complex has a significantly longer Cu–N(1), a shorter Cu–O(1) and a reduced chelate angle at copper. The origin of these differences of up to 0.2 Å in bond lengths and 8° in angle is most likely crystallographic rather than chemical.

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