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Synthesis and structural studies of some metal(II) complexes of 5-methyloxazolidine-4-carboxylic acid

Soon-Beng Teo*, **Chew-Hee Ng**
School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang (Malaysia)
Ernst Horn and **Edward R. T. Tiekink***
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, SA 5001 (Australia)

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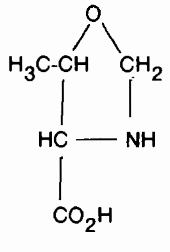
Abstract

The reactions of formaldehyde with the metal(II) chelates of L-threonine (metal = copper, nickel, cobalt and zinc) result in the formation of the metal(II) complexes of 5-methyloxazolidine-4-carboxylic acid. The copper(II) complex, $C_{10}H_{20}N_2O_8Cu$, is obtained from the recrystallization of its 3-hydroxymethyl derivative, $C_{12}H_{24}N_2O_{10}Cu$, which initially forms. $C_{10}H_{20}N_2O_8Cu$ crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 8.166(1)$, $b = 8.936(1)$, $c = 20.463(5)$ Å and $Z = 4$. The structure has been refined to $R = 0.021$ and $R_w = 0.021$ based on 1444 reflections with $I > 2.5\sigma(I)$. The geometry about copper is based on a square pyramid with a coordinated water in the apical position. The synthesized compounds are characterized by microanalysis, magnetic and thermal data as well as examinations of their electronic and infrared spectra.

Introduction

Although the reactions of formaldehyde with α-aminoacidato metal(II) complexes are well documented [1, 2], to date, there is no known account of such reactions with the corresponding threoninato metal(II) chelates.

The present paper describes the reactions of formaldehyde with bis(L-threoninato)-metal(II) (metal = copper, nickel, cobalt and zinc) which result in the formation of the metal(II) complexes of 5-methyloxazolidine-4-carboxylic acid (**1**)**. The copper(II) complex, however, is not derived directly from the reaction but is obtained from the recrystallization of its 3-hydroxymethyl derivative which is formed in the first instance from the reaction of formaldehyde with the copper(II) chelate of L-threonine.



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A full X-ray structural analysis of the copper(II) complex of **1** has been carried out and the results are reported along with a variety of microanalytical, thermal, magnetic and spectroscopic data for the synthesized compounds.

Experimental

Reagents

L-Threonine was used as supplied by B.D.H. Chemical Company. Formaldehyde was obtained as a 40% wt./vol. aqueous solution from May and Baker. The bis(L-threoninato)metal(II) complexes (M(L-threo)$_2$; M = Cu, Ni, Co, Zn) were prepared by previously established procedures [3, 4].

Preparation of compounds

Bis(3-hydroxymethyl-5-methyloxazolidine-4-carboxylato)copper(II), Cu(II)[3HOMe-5Me-OCA]$_2$

This compound is the direct product of the reaction of Cu(L-threo)$_2$ with formaldehyde in the

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*Authors to whom correspondence should be addressed.

The metal(II) complexes of **1 are abbreviated as M(II)[5MeOCA]$_2$ (M = Cu, Ni, Co, Zn).

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pH range 4.5–8.0. A typical preparative procedure is described as follows. A reaction mixture consisting of Cu(L-threo)$_2$ (2.7 g, 0.01 mol) and formaldehyde (20 cm^3) was diluted to 40 cm^3 with distilled water and then heated in a water bath at 40 °C.

The deep blue microcrystalline product which formed after a week was filtered, washed with cold acetone and ethanol and was finally dried under vacuum at 50 °C for 6 h. Yield 1.9 g (45%).

M(II)[5MeOCA]$_2$(M = Cu, Ni, Co, Zn)

Attempts to recrystallize Cu(II)[3HOMe-5MeOCA]$_2$ in a water–ethanol mixture have so far given rise to the isolation of blue crystals of Cu(II)[5MeOCA]$_2$.

The Ni(II), Co(II) and Zn(II) compounds of **1** were prepared by the reactions of formaldehyde with the corresponding threoninato complexes similar to that described above. The reactions carried out over the pH range 5.2–9.0 gave yields of 60% and the 3-hydroxymethyl species of these compounds have never been isolated.

Characterization

Microanalysis

All microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia. The results are shown in Table 1.

Magnetic moment measurement

The magnetic moments of the compounds (Table 2) were determined by the Gouy method [5, 6]. The magnetic field, calibrated with Hg[Co(CNS)$_4$], was produced by means of a Newport Type A electromagnet (with shimmed pole tips coned to 75 mm face diameter and special magnetic shunt).

Diamagnetic corrections were estimated from Pascal's constants.

Electrical spectral analysis

The diffuse reflectance spectra of the complexes (Table 2) were recorded on a Hitachi 330 Spectrophotometer. Analar magnesium oxide was the calibrant used.

Infrared spectral analysis

All IR spectra (data shown in Table 3) were recorded using a Nicolet 5MX FT-IR spectrometer with samples as KBr discs:

Thermal analysis

The thermograms for the decomposition of the compounds were recorded on a Dupont 990 Thermal analyser coupled to a Dupont 951 thermogravimetric analyser. The results are given in Table 4.

TABLE 1. Microanalysis results of M(II)[5MeOCA]$_2$ and Cu(II)[3HOMe-5MeOCA]$_2$

Compound	Formula	Calculated (%)			Found (%)		
		C	H	N	C	H	N
Cu(II)[5MeOCA]$_2$	$C_{10}H_{20}N_2O_8Cu$	33.38	5.60	7.79	33.43	5.45	7.74
Cu(II)[3HOMe-5MeOCA]$_2$	$C_{12}H_{24}N_2O_{10}Cu$	34.34	5.76	6.67	34.02	5.68	6.84
Ni(II)[5MeOCA]$_2$	$C_{10}H_{20}N_2O_8Ni$	33.80	5.70	7.89	33.60	5.50	7.94
Co(II)[5MeOCA]$_2$	$C_{10}H_{20}N_2O_8Co$	33.81	5.68	7.89	33.79	5.70	7.91
Zn(II)[5MeOCA]$_2$	$C_{10}N_{20}N_2O_8Zn$	33.21	5.57	7.75	33.33	5.57	7.75

TABLE 2. Magnetic moments and electronic spectra of M(II)[5MeOCA]$_2$ and Cu(II)[3HOMe-5MeOCA]$_2$

Compound	Magnetic moment μ_{eff} (BM)	Observed band (cm^{-1})	Tentative assignment of transition
Cu(II)[5MeOCA]$_2$	1.93	9800	$^2A_1 \leftarrow {}^2B_1$
		16700(sh)	$^2B_2 \leftarrow {}^2B_1$
		17240	$^2E \leftarrow {}^2B_1$
Cu(II)[3HOMe-5MeOCA]$_2$	1.93	9600	$^2A_1 \leftarrow {}^2B_1$
		16000(sh)	$^2B_2 \leftarrow {}^2B_1$
		17100	$^2E \leftarrow {}^2B_1$
Ni(II)[5MeOCA]$_2$	2.96	9800	$^3T_{1g} \leftarrow {}^3A_{2g}$
		15900	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$
		26300	$^3T_{2g} \leftarrow {}^3A_{2g}$
Co(II)[5MeOCA]$_2$	5.18	8600	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$
		16500(sh)	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$
		20400	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$

TABLE 3. IR data of M(II)[5MeOCA]$_2$ and Cu(II)[3HOMe-5MeOCA]$_2$

Compound	Infrared absorptions (cm^{-1})			
	ν(O–H)^a	ν(N–H)	ν(COO$_{asym}$)	ν(COO$_{sym}$)
Cu(II)[5MeOCA]$_2$	3500	3250^b	1610	1378
Cu(II)[3HOMe-5MeOCA]$_2$	3450		1600	1395
Ni(II)[5MeOCA]$_2$	3350	3240^b	1594	1408
Co(II)[5MeOCA]$_2$	3400	3240^b	1592	1400
Zn(II)[5MeOCA]$_2$	3400	3240^b	1591	1409

^{a}H$_2$O of coordination (broad band). ^{b}Doublet

TABLE 4. Thermal decomposition^a of M(II)[5MeOCA]$_2$ and Cu(II)[3HOMe-5MeOCA]$_2$

Compound	Range of decomposition (°C)	Mass loss(%)	Assignment of mass loss
Cu(II)[5MeOCA]$_2$	74–131 (115)^b	12.0	Loss of 2 water molecules (theoretical 11%)
Cu(II)[3HOMe-5MeOCA]$_2$	63–95 (88)^b	5.6	Loss of 1 water molecule of crystallization (theoretical 4%)
Ni(II)[5MeOCA]$_2$	140–224 (180)^b	10.5	Loss of 2 coordinated water molecules (theoretical 10.2%)
Co(II)[5MeOCA]$_2$	116–200 (156)^b	9.9	Loss of 2 structural water (theoretical 10.2%)
Zn(II)[5MeOCA]$_2$	110–168 (142)^b	9.6	Loss of 2 water molecule (theoretical 10.0%)

^{a}Only the first decompositions are shown due to their significance in determining the nature of the water molecules. ^{b}Figures in parentheses indicate the decomposition peaks.

Crystallography: determination of X-ray crystal structure of Cu(II)[5MeOCA]$_2$ $C_{10}H_{20}N_2O_8Cu$

Intensity data for a crystal with dimensions 0.18 × 0.31 × 0.38 mm were measured at room temperature on an Enraf-Nonius CAD4F diffractometer fitted with Mo K$_\alpha$ radiation, $\lambda = 0.7107$ Å. The ω:2θ scan technique was employed to measure a total of 1954 reflections such that θ_{max} was $\leqslant 25°$; some high-angle Friedel pairs were also included. No significant decomposition of the crystal occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption; analytical procedure max. and min. transmission factors were 0.715 and 0.636, respectively [7]. There were 1858 unique data of which 1444 satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis. Crystal data are listed in Table 5.

The structure was solved from the interpretation of the Patterson synthesis and refined by a full-matrix least-squares procedure based on F [7]. All non-hydrogen atoms were refined with an-

TABLE 5. Crystal data and refinement details for C$_{10}$H$_{20}$N$_2$O$_8$Cu

Formula	C$_{10}$H$_{20}$CuN$_2$O$_8$
Formula weight	359.8
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	8.166(1)
b (Å)	8.936(1)
c (Å)	20.463(5)
V (Å^3)	1493.1
Z	4
ρ_c (g cm^{-3})	1.601
F(000)	748
μ (cm^{-1})	14.70
Theta limits	1.5–25.0
Data collected	1954
Unique data	1858
Data with $I \geqslant 2.5\sigma(I)$	1444
R	0.021
k	10.6
g	0.0002
R_w	0.021
ρ_{max}(e Å^{-3})	0.2

isotropic thermal parameters and hydrogen atoms were located from a difference map and included in the model such that both their positional and thermal parameters were allowed to refine A weighting scheme of the form $w = k/[\sigma^2(F) + gF^2]$ was included and the refinement continued (for the preferred chirality) to final $R = 0\ 021$, $R_w = 0\ 021$ for $k = 10\ 6$ and $g = 0\ 0002$ The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0 20 e Å^{-3} Fractional atomic coordinates are listed in Table 6 and the numbering scheme employed is shown in Fig 1 which was drawn with ORTEP [8] The scattering factors for neutral Cu (corrected for f' and f'') were from ref 9 and those for the remaining atoms were as incorporated in SHELX76 [7]

TABLE 6 Fractional atomic coordinates ($\times 10^5$ for Cu, $\times 10^4$ for other atoms) for $C_{10}H_{20}N_2O_8Cu$

Atom	*x*	*y*	*z*
Cu	31518(5)	23563(4)	21464(2)
O(1)	2456(3)	332(3)	2395(1)
O(2)	1952(5)	−1119(3)	3244(1)
O(3)	668(4)	3272(3)	3829(2)
O(4)	3372(3)	4447(2)	1878(1)
O(5)	3475(4)	5923(3)	1012(1)
O(6)	1314(3)	1924(3)	306(1)
O(31)	5849(3)	1702(3)	2194(2)
O(41)	4168(4)	8824(3)	1376(2)
N(1)	2689(4)	2849(3)	3075(1)
N(2)	3021(4)	1932(3)	1191(1)
C(1)	2271(4)	99(3)	3004(2)
C(2)	2516(4)	1439(3)	3455(2)
C(3)	1035(5)	1715(4)	3913(2)
C(4)	1374(9)	1426(6)	4625(2)
C(5)	1128(6)	3624(5)	3184(2)
C(6)	3392(4)	4691(3)	1268(2)
C(7)	3332(4)	3329(3)	815(2)
C(8)	1895(5)	3422(3)	331(2)
C(9)	2318(6)	3949(6)	346(2)
C(10)	1412(5)	1417(5)	957(2)

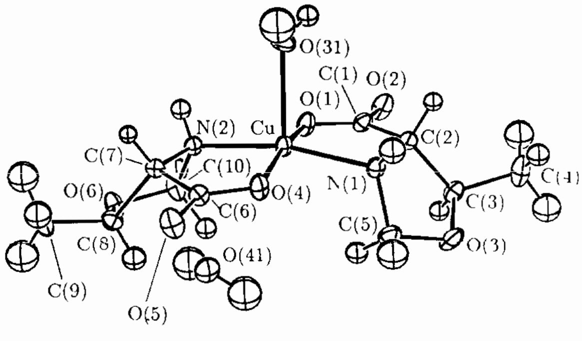

Fig 1 Molecular structure and crystallographic numbering scheme for $C_{10}H_{20}N_2O_8Cu$

Results and Discussion

The molecular structure of Cu(II)[5MeOCA]$_2$ (Fig 1) establishes the expected condensation of the formaldehyde and threonine moieties and the formation of a bidentate ligand All bond lengths within the ligands are within the range observed for similar complexes [1, 2, 10–12] The copper atom exists in a square pyramidal geometry with the basal plane defined by two N, O chelating ligands such that the oxygen donor atoms are *trans* The Cu–N(1) and Cu–O(1) bond lengths are again typical [1, 2, 10–12] The axial position in the coordination polyhedron is occupied by a coordinated water molecule and the copper atom lies 0 1272(4) Å out of the N_2O_2 basal plane in the direction of the coordinated water molecule Characteristically for Cu(II), the bond to the apical water molecule is longer than those to the donor atoms in the coordination square [12, 13] but the Cu-O(31) bond distance of 2 281(3) Å is shorter than those found in similar compounds [2, 10–13] Fractional atomic coordinates and selected interatomic parameters for the compound are listed in Tables 6 and 7, respectively

In the crystal lattice, there are several intermolecular contacts as might be expected The coordinated water molecule, however, does not participate in any significant intermolecular contact In contrast, the water molecule of crystallization forms several close contacts, these being 1 94 Å for H(41) O(5) such that the O(41)–H(41) O(5) angle is 160°, H(42) O(1′) of

TABLE 7 Selected bond distances (Å) and valence angles (°) for $C_{10}H_{20}N_2O_8Cu$

Cu–O(1)	1 963(2)	Cu–O(4)	1 956(2)
Cu–N(1)	1 987(3)	Cu–N(2)	1 994(3)
Cu–O(31)	2 281(3)	C(1)–O(1)	1 273(4)
C(1)–O(2)	1 222(4)	C(1)–C(2)	1 525(4)
C(2)–N(1)	1 487(4)	C(1)–C(3)	1 550(5)
C(3)–C(4)	1 506(6)	C(3)–O(3)	1 433(5)
O(3)–C(5)	1 407(5)	N(1)–C(5)	1 468(5)
C(6)–O(4)	1 267(4)	C(6)–O(5)	1 221(4)
C(6)–C(7)	1 530(4)	C(7)–N(2)	1 488(4)
C(7)–C(8)	1 538(5)	C(8)–C(9)	1 503(5)
C(8)–O(6)	1 422(4)	O(6)–C(10)	1 410(4)
N(2)–C(10)	1 472(5)		
O(1)–Cu–O(4)	168 4(1)	O(1)–Cu–N(1)	84 4(1)
O(1)–Cu–N(2)	93 6(1)	O(1)–Cu–O(31)	91 8(1)
O(4)–Cu–N(1)	94 3(1)	O(4)–Cu–N(2)	84 9(1)
O(4)–Cu–O(31)	99 7(1)	N(1)–Cu–N(2)	165 8(1)
N(1)–Cu–O(31)	101 5(1)	N(2)–Cu–O(31)	92 6(1)
Cu–O(1)–C(1)	116 0(2)	O(1)–C(1)–O(2)	124 4(3)
C(1)–C(2)–N(1)	111 2(3)	C(2)–C(3)–O(3)	104 2(3)
C(3)–O(3)–C(5)	105 9(3)	O(3)–C(5)–N(1)	105 6(3)
C(2)–N(1)–Cu	109 3(2)	C(2)–N(1)–C(5)	103 8(3)
C(5)–N(1)–Cu	114 5(2)	Cu–O(4)–C(6)	116 3(2)
O(4)–C(6)–C(7)	117 3(3)	C(6)–C(7)–N(2)	111 1(2)
C(7)–C(8)–O(6)	103 1(3)	C(8)–O(6)–C(10)	104 4(3)
O(6)–C(10)–N(2)	104 9(3)	C(10)–N(2)–Cu	115 2(2)

2.04 Å and O(42)–H(42) ··· O(1′) (where O(1′) is related by the symmetry operation: $x, 1+y, z$); and O(41″) ··· H(N2) of 2.30 Å where O(41″) ··· H(N2)–N(2) is 139° (O(41″) is related by the symmetry operation $x, -1+y, z$).

The room temperature magnetic moment of the compound as well as its electronic spectrum (Table 2) are in accord with those found for square pyramidal copper(II) complexes [5, 14–18]. Its IR spectrum exhibits a characteristic doublet due to the absorption of the =NH group at 3300–3160 cm^{-1}. However, absorptions due to =NH and –NH_2 groups are absent in the IR spectrum of Cu(II)[3HOMe-5MeOCA]$_2$ from which Cu(II)[5MeOCA]$_2$ is isolated when the former is recrystallized. The IR spectra of both compounds are very similar, having absorptions ascribed to coordinated water as well as carboxylate asymmetric and symmetric stretching frequencies (Table 3) and a triplet in the 1200–1080 cm^{-1} region characteristic of the oxazolidine ring system [16, 19]. Hence Cu(II)[3HOMe-5MeOCA]$_2$ is assigned a similar structure to that of Cu(II)[5MeOCA]$_2$, possessing an oxazolidine ring and an *N*-hydroxymethyl group.

The formation of the 3-hydroxymethyl derivative necessitates the initial loss of protons from the amino nitrogen of Cu(II)(L-threo)$_2$ with the ensuing electrophilic attack by formaldehyde molecules. Although such a phenomenon is known to occur in basic as well as non-basic media [1, 20], Cu(II)[3HOMe-5MeOCA]$_2$ appears to be the first example of a stable complex possessing an oxazolidine ring and an *N*-hydroxymethyl group to have been isolated. The room temperature magnetic moment of the compound is normal for high-spin copper(II) complexes [5, 14–18] and is consistent with the copper(II) ion being an orbitally non-degenerate state of the type $^2B_1$ or $^2A_1$, [14, 17]. Its electronic spectrum closely resembles those of the square pyramidal complexes [Cuen$_2$NH$_3$][BF$_4$]$_2$ [17] and [dihydro-1*H*,3*H*,5*H*-oxazolo-[3,4-*c*]oxazole-7*a*-carboxylato]copper(II) [16] and hence the observed bands are assigned similar transitions based on those assigned for the previous two compounds (Table 2). The empirical formula of the compound shows the presence of two water molecules. Since thermal analysis results (Table 4) indicate that the first weight loss (5%) closely corresponds to the elimination of a water of crystallization, it is surmised that the fifth coordination site in Cu(II)[3HOMe-5MeOCA]$_2$ is occupied by a water molecule.

The IR spectra of the Ni(II), Co(II) and Zn(II) derivatives of **1** show a close resemblance to that of Cu(II)[5MeOCA]$_2$, with similar absorptions in the diagnostic regions. These compounds are therefore postulated to have the same structure as that of the Cu(II) chelate. Their empirical formulae suggest that they each contain two molecules of water, the presence of which is evidenced by absorptions at 3650–3300 cm^{-1} in their IR spectra (Table 3). As thermal analysis has shown that these water molecules are not easily removed (Table 4), it is reasonable to assume that they are structural water which coordinate to the respective metal ions giving an octahedral arrangement about the metal ions.

The magnetic moments of the Ni(II) and Co(II) complexes are indicative of octahedral configuraions [5, 6, 15, 21]; so too are their solid reflectance spectra for which the absorptions bands are assigned transitions (as shown in Table 2) based on those found in the respective Ni(II) and Co(II) compounds having octahedral geometries [22].

Supplementary material

Tables of fractional atomic coordinates, thermal parameters, interatomic parameters and structure factor amplitudes are available on request from author E.R.T.T.

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