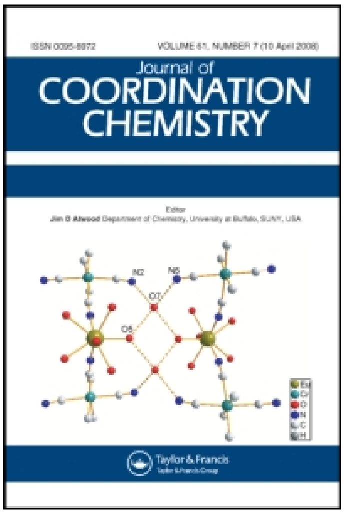

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Soon-Beng Teo[a]; Chew-Hee Ng[a]; Siang-Guan Teoh[a]; Chen Wei[b]
[a] School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia [b] Department of Chemsitry, University Malaya, Kuala Lumpur, Malaysia

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METAL(II) COMPLEXES OF *N,N'*-METHYLENEDI(*L*-PROLINE): INTER-LIGAND *N,N'*-METHYLENE BRIDGING OF BIS(*L*-PROLINATO)METAL(II) BY FORMALDEHYDE

SOON-BENG TEO,* CHEW-HEE NG, SIANG-GUAN TEOH

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

and CHEN WEI

Department of Chemsitry, University Malaya, Lembah Pantai, 59100 Kuala Lumpur, Malaysia

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The reaction of bis(*L*-prolinato)metal(II) (metal = cobalt, nickel, zinc) with formaldehyde leads to the formation of the respective metal(II) complexes of *N,N'*-methylenedi(*L*-proline), M(II) [My-Pro)$_2$], each of which possesses an *N,N'*-methylene bridge linking the chelated L-proline ligands.

KEYWORDS: bis(*L*-prolinato)metal(II), *N,N'*-methylene bridging, formaldehyde

INTRODUCTION

Investigations of the reactions of chelated α- and β-amino acids with formaldehyde have been extensively carried out.[1–8] By contrast, there has only been one reported instance of such reactions involving chelated cyclic amino acids, *viz*, the reaction of coordinated 4-hydroxy-*L*-proline with formaldehyde leading to the isolation of the metal(II) complexes of *N,N'*-methylenedi(4-hydroxy-*L*-proline), M(II)[My-(OH-Pro)$_2$].[9]

In this paper, we present results concerning the condensation reactions of the chelated cyclic amino acid *L*-proline with formaldehyde to yield metal(II) complexes of *N,N'*-methylenedi(*L*-proline), M(II)[My-(Pro)$_2$] (M = Co, Ni, Zn). X-ray structural determinations of M(II) [My-(Pro)$_2$] (M = Co, Ni) have been performed and the results are discussed herein.

EXPERIMENTAL

Preparation of bis(*L-prolinato)metal(II), M(II)(L-Pro)$_2$*

M(II)(L-Pro)$_2$ complexes were prepared by previously reported procedures.[10,11]

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* Author for correspondence.

Preparation of M(II) [My-(Pro)$_2$]

The preparation of Co(II) [My-(Pro)$_2$] is given as a typical procedure. The pH of a reaction mixture consisting of an aqueous solution of $CoCl_2 \cdot 6H_2O$ (1.2 g, 0.005 mol), *L*-proline (1.7 g, 0.01 mol) and 10 cm^3 of a 37% w/v solution of formaldehyde (0.12 mol) was raised to pH 7 by adding NaOH solution and then the reaction mixture allowed to evaporate slowly at room temperature. Wine-red crystals appeared after 2 weeks. These were washed with ethanol and finally dried *in vacuo* for 11 h. Yield 0.9 g (50%). *Anal. calc.* for $C_{11}H_{16}N_2O_4Ni \cdot 3H_2O$: C, 37.40; H, 6.26; N, 7.93%. Found: C, 37.45; H, 5.83; N, 7.93%. The other M(II) [My-(Pro)$_2$] (M = Ni, Zn) complexes were similarly prepared or by reacting M(II)(L-pro)$_2$ with formaldehyde.

Determination of crystal structure of $C_{11}H_{16}N_2O_4M(II) \cdot 3.5H_2O$

X-ray measurements at room temperature (27°C) were performed on single crystals of Co(II) [My-Pro)$_2$] and Ni(II) [My-Pro)$_2$] using a four-circle CAD4 diffractometer fitted with Mo-Kα radiation (λ = 0.71073 Å). Unit cell parameters were obtained from 25 strong reflections. Crystal data, data collection parameters and details of structure refinements for both crystals are summarized in Table 1.

Table 1 Crystal data and details of structure refinement for $C_{11}H_{16}N_2O_4M(II) \cdot 3.5H_2O$ (M = Co, Ni).

Complex	Co(II)	Ni(II)
Crystal system	Orthorhombic	Orthorombic
Space group	$P2_12_12$	$P2_12_12$
M_r	362.25	362.03
a (Å)	14.8536(3)	15.227(1)
b (Å)	15.2789(8)	14.8287(3)
c (Å)	7.021(1)	6.943(1)
Z	4	4
V (Å^3)	1593.4(3)	1567.8(3)
D_c (g cm^{-3})	1.510	1.534
μ (cm^{-1})	11.1	12.76
Crystal colour	Purple	Pale blue
Crystal description	Needles	Hexagonal prisms
Collection method	ω - 2θ	ω - 2θ
Absorption correction (T_{min})	92.25	97.98
Absorption correction (T_{max})	99.99	99.91
Data collected	1626	2448
Unique data	1608	1624
θ_{max} (°)	25	25
h	$-8 \rightarrow 0$	$0 \rightarrow 17$
k	$-17 \rightarrow 0$	$0 \rightarrow 8$
l	$-18 \rightarrow 0$	$-14 \rightarrow 18$
R	0.038	0.039
R_w ($w = [\sigma(F)^2]^{-1}$)	0.050	0.052
No. of parameters refined	210	198
Data with $I < 3\sigma(I)$	1425	1356
$(\Delta/\sigma)_{max}$	0.40	0.06
$(\Delta\rho)_{max}$ (e Å^{-3})	0.324	0.689

The $\omega - 2\theta$ scan mode was employed to measure reflections to $\theta_{max} = 25°$. Raw intensities were processed for Lorentz-polarization effects and for absorption.[12] Metal atom positions were obtained from Patterson synthesis and remaining atoms were located from difference Fourier maps. All non-hydrogen atoms were subjected to antisotropic refinement while the hydrogen atoms on the carbon atoms were generated geometrically with C-H at 0.95 Å and allowed to ride on their parent carbon atoms. Hydrogen atoms of the water molecules in the cobalt(II) complex were located from a difference map and their displacement parameters, B_{eq}, were fixed at 5 $Å^2$ while those in the nickel(II) complex were refined isotropically. Computations were performed using the MolEN package[13] on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors[14] were employed and anomalous dispersion corrections were incorparated.[15] Fractional atomic coordinates are listed in Table 2. Selected bond distances and valence angles are tabulated in Table 3 while the hrydrogen bond distances in the cobalt(II) and nickel(II) complexes are listed in Table 4. The molecular structure of the metal(II) complex with numbering scheme is shown in Figure 1.

RESULTS AND DISCUSSION

The molecular structure of Co(II) [My-$(Pro)_2$] (Figure 1) establishes the condensation of both proline moieties with formaldehyde and the formation of an *N,N'*-methylene bridged tetradentate ligand. Each proline moiety is chelated to the central cobalt atom via its amino nitrogen and carboxylato oxygen atoms.

The molecule has a distorted octahedral geometry about the central cobalt. atom. The carboxylic oxygen atoms occupy the axial positions while the equatorial plane is formed by two amino nitrogen atoms which are *cis* with respect to each other and two aqua-oxygen atoms. The equatorial plane is distorted by the strained four-membered ring N1-C11-N2-Co. The greatest deviations from ideal octahedral geometry are found for the O6-Co-N1 angle of 101.4(2)° and N1-Co-N2 angle of 65.8(2)°.

The methylene bridging of the two chelated *L*-proline moieties has resulted in the reduced N1-Co(1)-N2 angle (65.8(2)°) from the unstrained value of 90° and the lengthening of the Co(1)-N1 and Co(1)-N2 bonds (also observed for Co(II) [My-$(OH\text{-}Pro)_2$]).[9] However, the average Co-O (carboxylato oxygen atom) bond length (2.063 Å) is longer than that for Co(II) [My-OH-$Pro)_2$] (average bond length = 2.037 Å). Such an observation could be attributed to the effect of multiple hydrogen bonding at the carbonyl oxygen atoms O2 and O4 (see Table 4).

One of the pyrrolidine rings in both crystals has a significantly shortened C−C bond (C6−C7), 1.46(1) Å for the Ni complex; C7−C8, 1.45(1) Å for the Co complex). However, other bond lengths in the *L*-proline moieties are comparable with their corresponding bond lengths in Cu[N-CH_2OH-*L*-$pro)_2H_2O$],[16] Cu(*D,L*-$pro)_2$,[17] [Cr(*L*-$pro)_2OH]_2$[18] and Zn(*L*-$pro)_2$.[19]

In the Co complex, one of uncoordinated water molecules (O8) is located on a two-fold axis. All the water molecules in the crystal form an extensive hydrogen bonding network. The hydrogen bond distances are listed in Table 4.

Table 2 Atomic coordinate (× 10^5 for Co and Ni; × 10^4 for other atoms) and B_{eq} (Å^2) values with e.s.d's in parenthesis; B_{eq} = (4/3) × [a^2 × B(1,1) + b^2 × B(2,2) + c^2 × B(3,3) + ab(cos gamma) × B(1,2) + ac(cos beta) × B(1,3) × bc(cos alpha) × B(2,3)].

Atom	*x/a*	*y/b*	*z/c*	B*eq*
$C_{11}H_{16}N_2O_4Co \cdot 3.5\ H_2O$				
Co	14447(4)	16888(4)	36219(9)	2.10(1)
O1	635(4)	1319(2)	1364(6)	3.01(7)
O2	38(3)	1711(3)	-1406(5)	3.96(8)
O3	2280(2)	2191(3)	5685(5)	2.94(7)
O4	3694(2)	2520(3)	6393(6)	3.31(7)
O5	1357(3)	426(3)	4746(6)	4.01(9)
O6	373(2)	2243(3)	5032(6)	3.52(8)
O7	1285(4)	-811(3)	2000(8)	5.8(1)
O8	0	0	731(1)	5.9(2)
N1	1760(3)	2708(3)	1506(6)	2.56(8)
N2	2739(3)	1513(3)	2192(6)	2.52(8)
C1	1883(5)	3637(4)	2040(10)	4.1(1)
C2	941(5)	3980(4)	213(10)	5.5(2)
C3	408(4)	3456(4)	700(10)	4.2(1)
C4	1035(4)	2715(3)	65(8)	2.8(1)
C5	538(3)	1841(4)	-23(8)	2.9(1)
C6	2990(4)	697(4)	1230(10)	4.2(1)
C7	3470(5)	161(5)	2670(10)	5.9(2)
C8	3752(6)	758(4)	4170(10)	6.6(2)
C9	3450(3)	1677(3)	3616(7)	2.71(9)
C10	3111(3)	2174(4)	5374(7)	2.41(1)
C11	2581(4)	2245(4)	885(8)	3.6(1)
$C_{11}H_{16}N_2O_4Ni \cdot 3.5H_2O$				
Ni	17498(5)	14375(5)	35640(10)	1.82(1)
O1	1347(3)	652(3)	1308(7)	2.46(8)
O2	1739(4)	30(3)	-1448(6)	3.39(9)
O3	2262(3)	2238(3)	5662(6)	2.43(9)
O4	2537(3)	3661(3)	6450(7)	3.08(9)
O5	516(3)	1343(4)	4801(8)	3.6(1)
O6	2272(3)	346(3)	4968(7)	2.9(1)
O7	-761(3)	1222(4)	2088(9)	5.3(1)
O8	0	0	7380(10)	6.8(3)
N1	2761(3)	1730(3)	1514(8)	2.00(9)
N2	1556(3)	2700(3)	2157(7)	2.1(1)
C1	3693(5)	1849(5)	2060(10)	3.4(2)
C2	4039(6)	894(6)	2170(10)	4.6(2)
C3	3506(5)	374(5)	730(10)	3.6(2)
C4	2763(4)	1015(4)	40(10)	2.5(1)
C5	1882(5)	538(4)	-62(9)	2.4(1)
C6	734(5)	2946(5)	1160(10)	3.6(2)
C7	179(6)	3408(6)	2570(10)	5.3(2)
C8	755(5)	3669(7)	4220(10)	5.1(2)
C9	1679(4)	3410(4)	3661(9)	2.3(1)
C10	2208(4)	3075(4)	5392(9)	2.1(1)
C11	2318(5)	2565(4)	900(10)	3.1(1)

The molecular structure of the Ni(II) [My-$(Pro)_2$] is isostructural with that of Co(II) [My-$Pro)_2$]. However, the *a* and *b* axes in this complex are reversed.

As the infrared spectrum of the zinc(II) complex resembles those of Co(II) [My-$(Pro)_2$] and Ni(II) [My-$(Pro)_2$],[19] it is postulated to have the same structure as

Table 3 Selected bond distances (Å) and valence angles (°) for $C_{11}H_{16}N_2O_4M(II)\cdot 3.5H_2O$ (M = Co, Ni).

$C_{11}H_{16}N_2O_4Co\cdot 3.5H_2O$			
Co-O1	2.069(4)	N1-C11	1.474(8)
Co-O3	2.056(4)	N2-C6	1.467(8)
Co-O5	2.088(5)	N2-C9	1.475(7)
Co-O6	2.057(5)	N2-C11	1.467(8)
Co-N1	2.203(5)	C1-C2	1.50(1)
Co-N2	2.185(4)	C2-C3	1.51(1)
O1-C5	1.267(7)	C3-C4	1.532(9)
O2-C5	1.239(7)	C4-C5	1.528(9)
O3-C10	1.254(7)	C6-C7	1.49(1)
O4-C10	1.241(7)	C7-C8	1.45(1)
N1-C1	1.480(8)	C8-C9	1.52(1)
N1-C4	1.477(8)	C9-C10	1.534(8)
O1-Co-O3	173.1(2)	C4-N1-C11	113.8(5)
O1-Co-O5	90.1(2)	Co-N2-C6	122.8(4)
O1-Co-O5	91.8(2)	Co-N2-C9	107.3(3)
O1-Co-N1	78.5(2)	Co-N2-C11	93.0(3)
O1-Co-N2	97.2(2)	C6-N2-C9	106.0(5)
O3-Co-O5	96.7(2)	C6-N2-C11	113.6(5)
O3-Co-O6	88.5(2)	C9-N2-C11	114.1(5)
O3-Co-N1	94.8(2)	N1-C1-C2	103.4(6)
O3-Co-N2	80.7(2)	C1-C2-C3	106.0(7)
O5-Co-O6	98.7(2)	C2-C3-C4	105.5(6)
O5-Co-N1	157.1(2)	N1-C4-C3	104.5(5)
O5-Co-N2	96.6(2)	N1-C4-C5	111.9(5)
O6-Co-N1	101.4(2)	C3-C4-C5	113.3(5)
O6-Co-N2	162.3(2)	O1-C5-O2	124.7(6)
N1-Co-N2	65.8(2)	O1-C5-C4	117.7(5)
Co-O1-C5	118.9(4)	O2-C5-C4	117.6(6)
Co-O3-C10	117.6(4)	N2-C6-C7	105.9(6)
Co-N1-C1	122.2(4)	C6-C7-C8	106.6(7)
Co-N1-C4	108.2(3)	C7-C8-C9	108.0(7)
Co-N1-C11	92.1(3)	N2-C9-C8	103.1(5)
C1-N1-C4	104(5)	N2-C9-C10	113.3(4)
C1-N1-C11	115.7(5)	C8-C9-C10	110.3(6)
O3-C10-O4	125.2(6)	O4-C10-C9	116.5(5)
O3-C10-C9	118.2(5)	N1-C11-N2	108.3(5)
$C_{11}H_{16}N_2O_4Ni\cdot 3.5H_2O$			
Ni-O1	2.046(5)	N1-C11	1.473(9)
Ni-O3	2.034(5)	N2-C6	1.475(9)
Ni-O5	2.070(5)	N2-C9	1.494(8)
Ni-O6	2.050(5)	N2-C11	1.466(9)
Ni-N1	2.141(6)	C1-C2	1.51(1)
Ni-N2	2.133(5)	C2-C3	1.50(1)
O1-C5	1.264(9)	C3-C4	1.55(1)
O2-C5	1.241(8)	C4-C5	1.52(1)
O3-C10	1.258(8)	C6-C7	1.46(1)
O4-C10	1.243(8)	C7-C9	1.50(1)
N1-C1	1.48(1)	C8-C9	1.51(1)
N1-C4	1.475(9)	C9-C10	1.53(1)
O1-Ni-O3	174.4(2)	C4-N1-C11	113.8(6)
O1-Ni-O5	90.4(2)	Ni-N2-C6	123.3(5)
O1-Ni-O6	91.8(2)	Ni-N2-C9	106.3(4)
O1-Ni-N1	79.7(2)	Ni-N2-C11	92.5(4)

Table 3 (*Continued*)

O1-Ni-N2	96.2(2)	C6-N2-C9	105.1(6)
O3-Ni-O5	95.2(2)	C6-N2-C11	115.2(6)
O3-Ni-O6	88.4(2)	C9-N2-C11	114.4(6)
O3-Ni-N1	94.7(2)	N1-C1-C2	103.6(7)
O3-Ni-N2	82.5(2)	C1-C2-C3	105.1(7)
O5-Ni-O6	95.8(3)	C2-C3-C4	106.6(7)
O5-Ni-N1	160.4(2)	N1-C4-C3	103.2(6)
O5-Ni-N2	97.1(2)	N1-C4-C5	111.4(6)
O6-Ni-N1	101.4(3)	C3-C4-C5	111.9(6)
O6-Ni-N2	164.7(3)	O1-C5-O2	123.5(7)
N1-Ni-N2	67.5(2)	O1-C5-C4	118.2(6)
Ni-O1-C5	117.4(5)	O2-C5- C4	118.2(7)
Ni-O3-C10	116.4(5)	N2-C6-C7	107.1(7)
Ni-N1-C1	122.8(5)	C6-C7-C8	107.1(8)
Ni-N1-C4	108.6(4)	C7-C8-C9	106.4(8)
Ni-N1-C11	91.9(4)	N2-C9-C8	104.1(6)
C1-N1-C4	105.2(6)	N2-C9-C10	112.7(5)
C1-N1-C11	114.4(6)	C8-C9-C10	111.7(6)
O3-C10-C9	125.1(7)	O4-C10-C9	116.7(6)
O3-C10-C9	118.1(6)	N1-C11-N2	107.8(5)

Table 4 Hydrogen bond distances (Å) in the Co(II) and Ni(II) complexes.

Bond	Distance		Symmetry Operation*
	Co(II)	Ni(II)	
O2—O6a	2.677(7)	2.659(8)	a: $x, y, z - 1$
O2—O8a	2.767(5)	2.771(7)	
O2—O8b	2.767(5)	2.771(7)	b: $x, y, z - 1$
O4—O6c	2.712(6)		c: $0.5 - x, 0.5 + y, 1 - z$
O4—O7d	2.789(7)		d: $0.5 + x, 0.5 - y, 1 - z$
O4—O6d		2.701(7)	
O4—O7c		2.788(8)	
O5—O8e	2.778(7)	2.790(9)	e: x, y, z
O5—O7	2.702(8)	2.714(9)	

* Here, a,b,c,d and e refer to the symmetry operations given.

the latter two complexes. This is corroborated by the excellent agreement of the microanalytical data with the proposed molecular formula.[19]

The formation of the above M(II)[My-(Pro)$_2$] must involve the initial *N*-hydroxymethylation of M(II) (*L*-pro)$_2$ by formaldehyde, a phenomenon which has been widely demonstrated in the reactions of amino acid chelates with formaldehyde.[1–8,16] In the present reaction, it is likely that the *N*-hydroxymethyl substituent of one chelated *L*-proline condenses with the proton of the other chelated *L*-proline to yield the inter-ligand *N,N'*-methylene bridge.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of anisotropic, thermal parameters, positional and thermal parameters for the H atoms, and structure factor amplitudes are available on request from the authors.

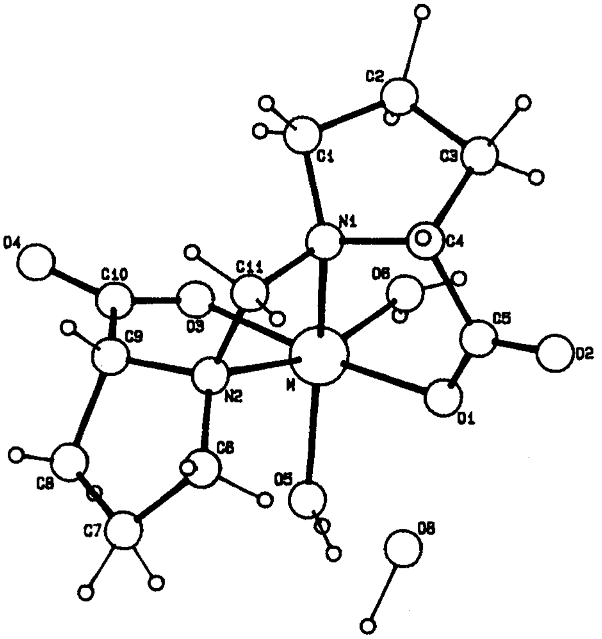

Figure 1 A perpective view of the molecule $C_{11}H_{16}N_2O_4M \cdot 3.5H_2O$ (M = Co, Ni).

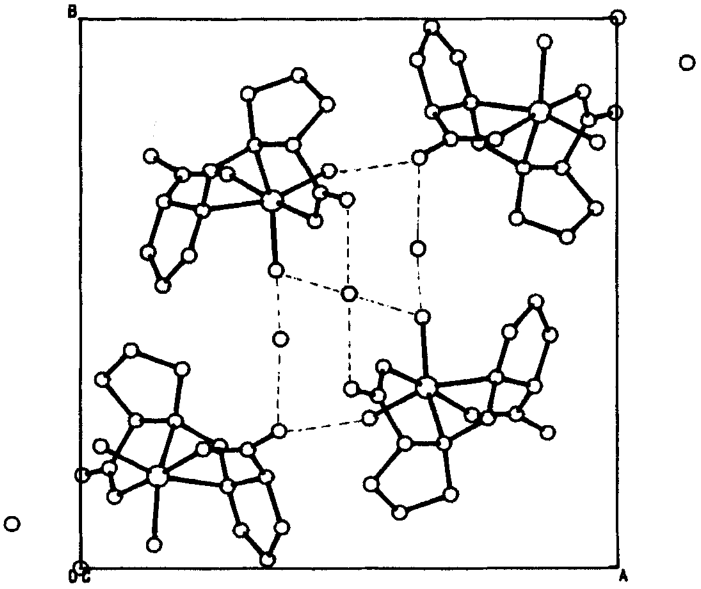

Figure 2 Diagram showing the unit cell contents projected down the *c* axis. Intermolecular hydrogen bonding is indicated by broken lines.

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