Bull. Chem. Soc. Jpn., **55**, 3135—3137 (1982)

The Structure of Dichloro(4-hydroxy-L-proline)cadmium(II)

Yasuhiko YUKAWA,* Yoshie INOMATA, Toshio TAKEUCHI,
Mamoru SHIMOI,† and Akira OUCHI†

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102
†Department of Chemistry, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received November 4, 1981)

An X-ray diffraction study of the title complex has been carried out. The crystal is monoclinic, with the space group $P2_1$; $Z=2$; $a=8.196(4)$, $b=7.275(3)$, $c=7.740(4)$ Å, $\beta=103.73(4)°$. Full-matrix least-squares refinements have led to the final R value of 0.030. The structure consists of one-dimensional polymers bridged by chlorine atoms and a carboxyl group. Four chlorine atoms coordinate to a cadmium atom and form a square plane. The planes extend in the direction of the b axis like an infinite folding screen, sharing opposite edges. From the trough positions in the zigzag structure, the carboxyl oxygen atoms of 4-hydroxy-L-proline coordinate forkedly to two cadmium atoms. The ligand is a zwitter ion in the complex.

Amino acids such as 4-hydroxy-L-proline (Hhpro) and proline are important to biochemists who investigate the constitution and configuration of proteins. The crystal structure of Hhpro has been determined by Donohue and Trueblood[1] and by Koetzele *et al.*[2]

There are few studies, however, about metal complexes with Hhpro. In this work a cadmium complex with Hhpro was prepared. Its crystal and molecular structure was determined in order to investigate how Hhpro coordinates to the metal.

Experimental

Preparation of Dichloro(4-hydroxy-L-proline)cadmium(II); $CdCl_2(Hhpro)$. To an aqueous solution of 2.62 g (0.02 mol) of Hhpro, 4.57 g (0.02 mol) of $CdCl_2\cdot2.5H_2O$ was added. Then the solution (pH 3.7) was stirred for several hours on a water bath at 60—70 °C. Clear colorless prisms were obtained by standing at room temperature; they were dried *in vacuo* at 50 °C for several hours.

Found: C, 19.08; H, 2.86; N, 4.49; Cl, 22.40; Cd, 35.9%. Calcd for $CdCl_2(C_5H_9NO_3)$: C, 19.10; H, 2.88; N, 4.45; Cl, 22.55; Cd 35.75%.

X-Ray Measurements. The crystal data are given in Table 1.

The reflections were collected by the θ-2θ scan technique ($2\theta\leqq70°$) on a Philips PW 1100 automated four-circle diffractometer. The 1990 independent reflections with $|F_o|\geqq3\sigma(|F_o|)$ were used for the structure refinement. The intensities were corrected for Lorentz and polarization factors, but no correction was made for the absorption because of the low magnitude of $\mu r(=0.42)$. All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using the local versions of UNICS[3] and LINUS.[4] The atomic scattering factors were taken from tables.[5]

Structure Determination. The structure was solved by a heavy-atom method. The positions of the cadmium atom and chlorine atoms were obtained from a three-dimensional Patterson function, while the positions of all the other non-hydrogen atoms were successively located by Fourier syntheses. Since the positions of few hydrogen atoms were obtained by a difference Fourier syntheses, all of the positions were calculated and fixed. Their isotropic temperature factors were all assumed to be 5.0 Å^2. Since the absolute configuration of Hhpro was known, the structure analysis was based on the configuration.

Table 1. Crystal data

$CdCl_2(C_5H_9NO_3)$	F.W.$=314.44$
Monoclinic	Space group $P2_1$
$a=8.196(4)$ Å	
$b=7.275(3)$ Å	$\beta=103.73(4)°$
$c=7.740(4)$ Å	
$Z=2$	$U=448.3(4)$ Å^3
$D_m=2.35$ g cm^{-3}	$D_x=2.33$ g cm^{-3}
μ(Mo $K\alpha$)$=29.7$ cm^{-1}	

The crystal used for data collection showed quite severe extinction, and full-matrix least-squares refinements including an extinction correction were carried out, using LINUS. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.06\times|F_o|)^2]$.

In the last cycle of the refinement with anisotropic temperature factors for all non-hydrogen atoms, all the parameter shifts were less than one-third of the corresponding standard deviations. The final R value ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0.030.

IR Measurements. The infrared spectra of the samples were obtained by means of a Hitachi EPI-G2 type infrared spectrophotometer, using Nujol mull and KBr pellets.

Results and Discussion

The final atomic parameters are listed in Table 2,[6] the interatomic distances in Table 3, and the bond angles in Table 4. The perspective drawing of the complex and the numbering scheme of atoms are shown in Fig. 1.

The complex has the structure of a one-dimensional polymer bridged by chlorine atoms and carboxyl oxygen atoms as shown in Fig. 2. Four chlorine atoms coordinate to a cadmium atom and form a square plane within 0.002 Å. The cadmium atom deviates 0.04 Å from the plane. The planes extend zigzag in the direction of the b axis like an infinite folding screen, sharing opposite edges. The dihedral angle between adjacent planes is 142°. From the trough positions in the zigzag folding structure the carboxyl oxygen atoms of Hhpro coordinate forkedly to two cadmium atoms. Therefore the cadmium atom has octahedral coordination.

The bond distances of the coordinating Hhpro are not so different from those of the free molecule. The interatomic distance between N and O(2) is rather short, 2.62 Å. Koetzele *et al.*[2] carried out a neutron diffraction study of Hhpro. Their results also show

Table 2. Final positional parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for hydrogen atoms) and equivalent isotropic temperature factors ($B_{eq}/Å^2$), with the estimated standard deviations

Atom	x	y	z	$B_{eq}/Å^2$
Cd	23.7 (5)	0	−38.8 (5)	1.6
Cl(1)	2125 (1)	−2494 (4)	−502 (1)	2.1
Cl(2)	2315 (1)	2489 (4)	1173 (1)	1.8
O(1)	−273 (4)	1025 (5)	−2973 (4)	2.1
O(2)	81 (4)	4083 (5)	−2780 (4)	2.0
O(3)	5883 (4)	1508 (6)	−3728 (5)	3.0
N	2705 (4)	4107 (6)	−4153 (6)	2.5
C(1)	389 (3)	2511 (7)	−3292 (3)	1.4
C(2)	1645 (4)	2413 (6)	−4484 (4)	1.7
C(3)	2917 (5)	842 (7)	−4060 (6)	2.3
C(4)	4530 (5)	1645 (6)	−2856 (5)	2.0
C(5)	4119 (5)	3659 (7)	−2590 (6)	2.5
H(21)	88	222	−581	
H(31)	317	29	−527	
H(32)	244	−27	−338	
H(41)	492	92	−160	
H(51)	374	383	−136	
H(52)	519	452	−257	
H(N1)	199	525	−386	
H(N2)	318	442	−530	

The numbering scheme of hydrogen atoms is based on the number of the atom attached to the hydrogen atom.

Table 3. Interatomic distances with the estimated standard deviations in parentheses

	l/Å		l/Å
Cd–Cd^{I}	3.638 (1)	C(1)–C(2)	1.538 (4)
		C(2)–N	1.494 (6)
Cd–Cl(1)	2.585 (2)	C(2)–C(3)	1.529 (6)
Cd–Cl(2)	2.617 (2)	C(3)–C(4)	1.540 (5)
Cd–Cl(1)^{I}	2.636 (2)	C(4)–O(3)	1.432 (6)
Cd–Cl(2)^{II}	2.643 (2)	C(4)–C(5)	1.529 (6)
Cd–O(1)	2.347 (3)	C(5)–N	1.499 (5)
Cd–O(2)^{II}	2.303 (3)	N···O(2)	2.615 (5)
O(1)–C(1)	1.260 (6)		
O(2)–C(1)	1.256 (6)	N···O(3)^{III}	2.825 (6)

Key to symmetry operations: I. $-x$, $0.5+y$, $-z$; II. $-x$, $-0.5+y$, $-z$; III. $1.0-x$, $0.5+y$, $-1.0-z$.

Table 4. Bond angles, with the estimated standard deviations in parentheses

	ϕ/°		ϕ/°
Cl(1)–Cd–Cl(2)	95.17(6)	C(3)–C(2)–N	103.9(3)
Cl(1)–Cd–O(1)	90.47(8)	C(2)–C(3)–C(4)	106.9(3)
Cl(1)–Cd–O(2)^{I}	95.97(9)	C(3)–C(4)–O(3)	109.8(3)
Cl(2)–Cd–O(1)	91.60(8)	C(3)–C(4)–C(5)	105.1(3)
Cl(2)–Cd–O(2)^{I}	92.61(9)	C(5)–C(4)–O(3)	110.5(4)
O(1)–C(1)–O(2)	126.3(3)	C(4)–C(5)–N	104.6(3)
O(1)–C(1)–C(2)	117.3(4)	C(5)–N–C(2)	105.4(3)
O(2)–C(1)–C(2)	116.4(4)		
C(1)–C(2)–C(3)	115.2(3)	C(4)–O(3)···N^{II}	141.9(3)
C(1)–C(2)–N	107.7(3)		

Key to symmetry operations: I. $-x$, $-0.5+y$, $-z$; II. $1.0-x$, $-0.5+y$, $-1.0-z$.

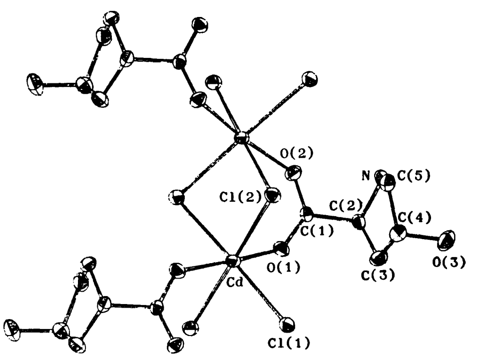


Fig. 1. The perspective drawing of $CdCl_2$(Hhpro) and the numbering scheme of non-hydrogen atoms.

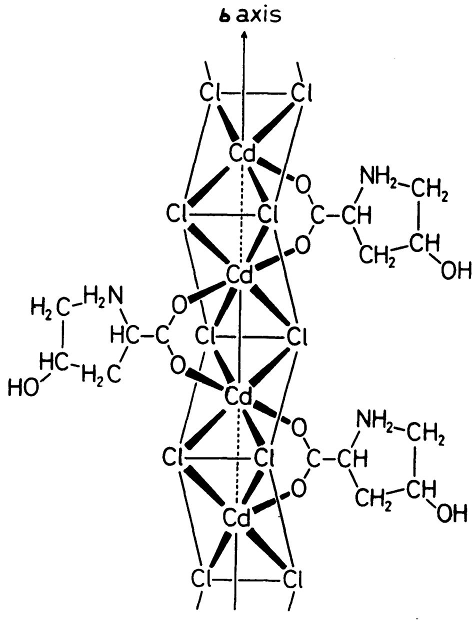


Fig. 2. The sketch of the structure.

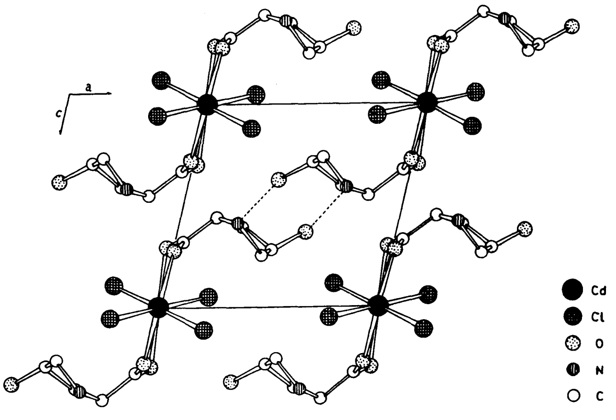
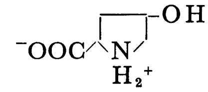


Fig. 3. The projection of the structure along the b axis. ------: Hydrogen bonding.

that the nitrogen atom in the pyrrolidine ring is close to the carboxyl oxygen atom. They have reported that an unusual intramolecular hydrogen bond exists between these atoms: this intramolecular hydrogen bond remains after the coordination to cadmium atoms.

In the free molecule the four atoms of a pyrrolidine ring are nearly coplanar, except for the carbon atom carrying a hydroxyl group. On coordination, however, the pyrrolidine ring is bent on the line from N to C(3) and C(4) and C(5) atoms deviate from the best-plane of the pyrrolidine ring. Some bond angles, N–C(2)–C(3), N–C(2)–C(1) and C(2)–N–C(5), are smaller than those of the free molecule, and other angles, C(1)–C(2)–C(3) and C(3)–C(4)–C(5), are larger.

The projection along the b axis is given in Fig. 3. The zigzag folding screen is parallel to the b axis with the cadmium atoms lying on the corners and on the middle of the b axis of the unit cell. It is connected with the neighboring one by hydrogen bonds between the nitrogen atom in the pyrrolidine ring and the hydroxyl oxygen atom, as indicated with broken lines in Fig. 3. Thus, a sheet forms parallel to the (101) plane. The whole structure is made up of these sheets, stacked together, only with van der Waals' contacts.

There are a few infinite folding screen structures: $CuCl_2$(1,2,4-triazole),[7] Cu(benzoato)$_2$·3H_2O,[8] $CuCl_2$-(*N*-nitrosodimethylamine).[9] Each ligand of these complexes has two adjacent atoms which coordinate to form the structure favorably. In the case of Hhpro there is the nitrogen atom of pyrrolidine ring as a coordinating atom besides the carboxyl oxygen atoms. In general both of them coordinate to a metal, but only carboxyl group coordinates to cadmium atoms in $CdCl_2$(Hhpro). Since the preparation conditions of the complex were at rather low pH, the Hhpro behaves as a zwitter ion,  ^{-}OOC–$\overset{}{\underset{H_2^+}{N}}$–OH, and the nitrogen atom will not be able to coordinate to a cadmium atom. This suggestion was confirmed by infrared spectra.

The infrared spectra of the free ligand, the deuterated ligand, $CdCl_2$(Hhpro), and the deuterated complex are shown in Fig. 4. The deuterated compounds were obtained by recrystallization from 99.75% D_2O. It has been established that the free ligand molecule is a zwitter ion, and the peaks in the region above 3000 cm^{-1} shift, by deuteration, from 2500 cm^{-1} to 2000 cm^{-1}. These peaks are assigned to an OH stretching vibration and to NH stretching vibrations.[10] The peaks at 1637 cm^{-1} and 1429 cm^{-1} shift to 1133 cm^{-1} and 993 cm^{-1}, respectively. In $CdCl_2$(Hhpro), similarly, the peaks in the region above 3000 cm^{-1} shift from 2500 cm^{-1} to 2250 cm^{-1} (the peak at 3475 cm^{-1} is assigned to an OH stretching vibration, and the others are NH stretching vibrations[11,12]), and the peaks at 1532 cm^{-1} and 1360 cm^{-1} shift to 1145 cm^{-1} and 1000 cm^{-1}, by deuteration respectively. If the ligand in $CdCl_2$(Hhpro) contained NH instead of NH_2^+, only one bending vibration should be observed. Since two corresponding peaks of NH bending vibrations are observed, the ligand can be regarded as a zwitter ion.

The characterization study of some metal complexes with Hhpro has been carried out in our group and will be published soon.

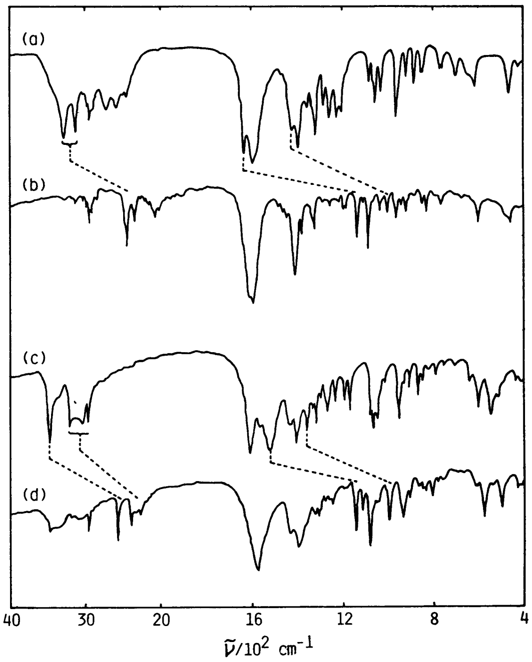


Fig. 4. Infrared spectra of (a) Hhpro, (b) the deuterated ligand, (c) $CdCl_2$(Hhpro), and (d) the deuterated complex. The shifts of the peaks by deuteration are indicated by the dotted lines.

The authors wish to express their thanks to Professor Yoichi Iitaka for the X-ray diffractometer measurements, and to Dr. Shoichi Sato, The University of Tokyo for the helpful discussions. They would also like to thank Dr. F. S. Howell of Sophia University for correcting this manuscript. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 547045 from the Ministry of Education, Science and Culture.

References

1) J. Donohue and K. N. Trueblood, *Acta Crystallogr.*, **5**, 419 (1952).

2) T. F. Koetzele, M. S. Lehmann, and W. C. Hamilton, *Acta Crystallogr., Sect. B*, **29**, 231 (1973).

3) "The Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

4) LINUS, H. Coppens and W. C. Hamilton, *Acta Crystallogr., Sect. A*, **26**, 71 (1970).

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, U. K. (1974), Vol. IV.

6) The final thermal parameters and the final F_o-F_c table are deposited as Document No. 8246 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

7) J. A. J. Jarvis, *Acta Crysrtallogr.*, **15**, 964 (1962).

8) H. Koizumi, K. Osaki, and T. Watanabe, *J. Phys. Soc. Jpn.*, **18**, 117 (1963).

9) U. Klement, *Acta Crystallogr., Sect. B*, **25**, 2460 (1969).

10) M. J. Deveney, A. G. Walton, and J. L. Koenig, *Biopolymers*, **10**, 615 (1971).

11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 3rd ed, Chapman and Hall, London (1975), pp. 107—128, 263—276.

12) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Now York (1978), pp. 305—312.