July, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2125—2128 (1983) 2125

Structure and Properties of Dichloro(L-proline)cadmium(II) Hydrate

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(Received December 8, 1982)

An X-ray diffraction study of the title complex has been carried out. The crystal is orthorhombic, with the space group $P2_12_12_1$; $Z=4$, $a=10.021(3)$, $b=13.562(4)$, $c=7.298(3)$ Å. Block-diagonal least-squares refinements have led to the final R value of 0.035. The structure is very similar to that of dichloro(4-hydroxy-L-proline)cadmium(II), which has a one-dimensional polymer bridged by chlorine atoms and a carboxyl group like an infinite folding screen. The thermal behavior is, however, different from that of dichloro(4-hydroxy-L-proline)cadmium(II). The difference is likely to be due to a difference of the crystal structure, whether it contains intermolecular hydrogen bonds or not.

Amino acids such as 4-hydroxy-L-proline (Hhpro) and proline (Hpro), which have a pyrrolidine ring, are important to biochemists who investigate the constitution and configuration of proteins. There are few studies, however, about metal complexes with Hhpro and Hpro. The crystal and molecular structure of $CdCl_2$(Hhpro) was previously determined in order to investigate how Hhpro coordinates to the metal.[1]

In this work, the complex with Hpro was prepared and characterized, including the determination of its structure. These results were compared with those from $CdCl_2$(Hhpro).

Experimental

Preparation of Dichloro(L-proline)cadmium(II) Hydrate; $CdCl_2(Hpro)\cdot H_2O$. The complex was prepared in almost the same way as used for $CdCl_2$(Hhpro);[1] equimolar amounts of $CdCl_2\cdot 2.5H_2O$ and Hpro were mixed in aqueous solution, and the solution was adjusted to pH 4 with *ca.* 2 mol dm^{-3} HCl. All chemicals used were reagent grade. The obtained colorless prisms were air-dried.

Found: C, 18.91; H, 3.01; N, 4.58; Cl, 22.45; Cd, 35.4%. Calcd for $CdCl_2(C_5H_9NO_2)\cdot H_2O$: C, 18.98; H, 3.50; N, 4.43; Cl, 22.41; Cd, 35.52%.

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

The crystal for data collection was shaped into a sphere ($\phi=0.34$ mm) and covered by cyanoacrylate resin to prevent the loss of H_2O from the crystal. The reflections were collected by the ω-2θ scan technique ($2\theta<65°$) on a Philips PW 1100 automated four-circle diffractometer, using Mo $K\alpha$ radiation (0.7107 Å). The 1464 independent reflections with $|F_o|>3\sigma(|F_o|)$ 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 μr (=0.45). All the calculations were carried out on a HITAC M-200H computer at the Computer Center of the University of Tokyo, using the local version of UNICS.[2] The atomic scattering factors were taken from tables.[3]

TABLE 1. CRYSTAL DATA

$CdCl_2(C_5H_9NO_2)\cdot H_2O$	F.W.=316.45
Orthorhombic	Space group $P2_12_12_1$
$a=10.021(3)$ Å	
$b=13.562(4)$ Å	
$c=7.298(3)$ Å	
$Z=4$	$U=991.8(6)$ Å^3
$D_m=2.13$ g cm^{-3}	$D_x=2.12$ g cm^{-3}
μ(Mo $K\alpha$)$=26.7$ cm^{-1}	

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 only a 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 Hpro was known, the structure analysis was based on this configuration.

All other positions and thermal parameters were refined by a repeated block-diagonal least-squares method. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.04\times|F_o|)^2]$. 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 0.035.

The Other Measurements. The simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were carried out with a Rigaku Denki "Thermoflex" M-8075 using a sample weighing about 10 mg in each operation; the heating rate was 5 °C min^{-1} in air and α-alumina was used as the reference.

The infrared spectra of the samples were obtained by means of a Hitachi EPI-G2 infrared spectrophotometer, using Nujol and hexachloro-1,3-butadiene mull, and KBr disks.

Results and Discussion

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

The complex has a very similar structure to that of $CdCl_2$(Hhpro); it consists of a one-dimensional polymer bridged by chlorine atoms and carboxyl oxygen atoms. The four chlorine atoms which coordinate to a cadmium atom are almost on a plane; the deviations of these atoms from the calculated best plane are shown in Table 5. The planes extended zigzag in the direction of the c axis like an infinite folding screen, sharing opposite edges. The dihedral angle between adjacent planes is 146°. From the trough positions in the zigzag folding structure, the two carboxyl oxygen atoms of Hpro coordinate to the two cadmium atoms. All the angles around the cadmium

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

Atom	x	y	z	$B_{\rm eq}$/Å^2
Cd	2463.0(4)	21.2(2)	3333.7(5)	1.81
Cl(1)	4324(1)	344(1)	872(2)	2.12
Cl(2)	3726(2)	1026(1)	5844(2)	2.60
O(1)	1299(5)	1414(4)	2398(6)	2.99
O(2)	1386(5)	1359(4)	−652(5)	2.64
N	−919(6)	2225(4)	−1214(7)	3.05
C(1)	831(6)	1536(4)	799(8)	2.14
C(2)	−540(7)	2027(6)	706(9)	3.00
C(3)	−1607(7)	1309(10)	1353(14)	5.71
C(4)	−1929(10)	719(9)	−291(21)	6.94
C(5)	−1835(9)	1422(7)	−1815(15)	5.23
O(W)	896(8)	2516(6)	5890(8)	5.43
H(21)[b)]	−48	269	152	
H(31)	−248	170	184	
H(32)	−123	84	243	
H(41)	−292	41	−20	
H(42)	−122	12	−46	
H(51)	−144	106	−302	
H(52)	−281	172	−213	
H(N1)	−50	254	−231	
H(N2)	−144	274	−53	

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{\rm eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$. b) 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

Interatomic distance	l/Å	Interatomic distance	l/Å
Cd-Cd$^{\rm I}$	3.650(3)	C(1)-C(2)	1.528(10)
		C(2)-N	1.477(11)
Cd-Cl(1)	2.627(3)	C(2)-C(3)	1.520(13)
Cd-Cl(2)	2.611(3)	C(3)-C(4)	1.479(20)
Cd-Cl(1)$^{\rm I}$	2.624(3)	C(4)-C(5)	1.468(19)
Cd-Cl(2)$^{\rm II}$	2.596(3)	C(5)-N	1.490(11)
Cd-O(1)	2.323(5)	N···O(2)	2.624(9)
Cd-O(2)$^{\rm I}$	2.319(5)		
O(1)-C(1)	1.268(8)	N···O(W)$^{\rm III}$	2.816(11)
O(2)-C(1)	1.220(8)		

Key to symmetry operations in this table and subsequent tables: I. $0.5-x$, $-y$, $0.5+z$; II. $0.5-x$, $-y$, $-0.5+z$; III. x, y, $-1.0+z$.

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

Bond angle	ϕ/°	Bond angle	ϕ/°
Cl(1)-Cd-Cl(2)	92.80(5)	O(2)-C(1)-C(2)	117.2(6)
Cl(1)-Cd-O(1)	91.17(13)	C(1)-C(2)-C(3)	109.9(7)
Cl(1)-Cd-O(2)$^{\rm I}$	89.97(12)	C(1)-C(2)-N	110.7(6)
Cl(2)-Cd-O(1)	91.45(13)	C(3)-C(2)-N	103.3(7)
Cl(2)-Cd-O(2)$^{\rm I}$	87.49(13)	C(2)-C(3)-C(4)	104.4(1.0)
Cd-Cl(1)-Cd$^{\rm II}$	88.09(4)	C(3)-C(4)-C(5)	104.4(1.0)
Cd-Cl(2)$^{\rm II}$-Cd$^{\rm II}$	89.02(5)	C(4)-C(5)-N	107.0(1.0)
O(1)-C(1)-O(2)	127.2(6)	C(5)-N-C(2)	107.7(6)
O(1)-C(1)-C(2)	115.5(6)		

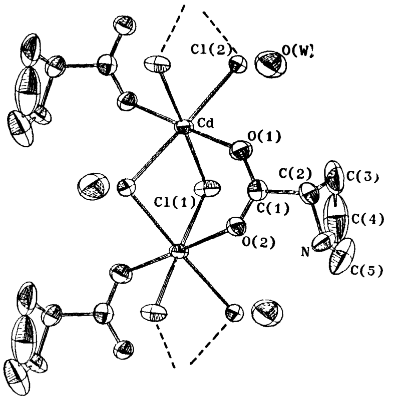


Fig. 1. The perspective drawing of $\mathrm{CdCl_2(Hpro)\cdot H_2O}$ and the numbering scheme of non-hydrogen atoms.

atom with four chlorine atoms and two carboxyl oxygen atoms are approximately 90°. The average bond distance of Cd–Cl is 2.61 Å, and that of Cd–O is 2.32 Å. Thus the cadmium atom has octahedral coordination. The bond distance of Cd–Cl and the angle of Cd–Cl–Cd (=88°) are comparable with those of $\mathrm{CdCl_2(biuret)_2}$, which consists of an infinite linear ribbon of $\mathrm{CdCl_2}$: Cd–Cl, 2.55(1), 2.62(1) Å; Cd–Cl–Cd, 91.5(3)°.[5)] The ligand is a zwitter ion in the complex.

In $\mathrm{CdCl_2(Hhpro)}$, there are intermolecular hydrogen bonds between the nitrogen atom in the pyrrolidine ring and the hydroxyl oxygen atom. In contrast, $\mathrm{CdCl_2(Hpro)\cdot H_2O}$ does not contain any intermolecular hydrogen bonds. Thus the pyrrolidine ring is not fixed and the positions far from the coordination atoms in Hpro have rather large temperature factors. Therefore, the calculated bond lengths of C(3)–C(4) (1.479(20) Å) and C(4)–C(5) (1.468(19) Å) are slightly shorter than the normal C–C bond length. A water molecule is connected to the nitrogen atom in the pyrrolidine ring by hydrogen bonding, instead of by intermolecular hydrogen bonds.

On coordination, the pyrrolidine ring in Hpro 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. The intramolecular hydrogen bond exists between N and O(2).

The projections of $\mathrm{CdCl_2(Hpro)\cdot H_2O}$ along the c axis and of $\mathrm{CdCl_2(Hhpro)}$ along the b axis are given in Fig. 2. In both cases, the zigzag folding screen is parallel to 2_1 axis. In $\mathrm{CdCl_2(Hhpro)}$ it is connected with the neighboring one by hydrogen bonds between the nitrogen atom in the pyrrolidine ring and the hydroxyl oxygen atom; a sheet forms parallel to the (101) plane. In $\mathrm{CdCl_2(Hpro)\cdot H_2O}$, there are no such hydrogen bonds and individual zigzag folding

Table 5. Least-squares planes and the deviations of atom (l/Å)

Plane(1) [Cl(1), Cl(2), $\mathrm{Cl(1)^{I}}$, $\mathrm{Cl(2)^{II}}$]
$-0.4971X+0.8181Y-0.2892Z+1.954=0$
Cl(1), −0.0029; Cl(2), 0.0029; $\mathrm{Cl(1)^{I}}$, −0.0029; $\mathrm{Cl(2)^{II}}$, 0.0029
(Cd, 0.0471)

Plane(2) [O(1), O(2), C(1), C(2)]
$-0.4199X-0.9075Y+0.01406Z+2.254=0$
O(1), −0.0079; O(2), −0.0082; C(1), 0.0223; C(2), −0.0059

Plane(3) [Cd, O(1), O(2), $\mathrm{Cd^{II}}$]
$-0.8510X-0.5250Y-0.01089Z+2.139=0$
Cd, −0.0033; O(1), 0.0055; O(2), −0.0056; $\mathrm{Cd^{II}}$, 0.0035
(C(1), 0.3301)

X, Y, and Z are coordinates expressed by the following equation:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} a & b\cos\gamma & c\cos\beta \\ 0 & b\sin\gamma & -c\cos\alpha^*\sin\beta \\ 0 & 0 & c\sin\alpha^*\sin\beta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

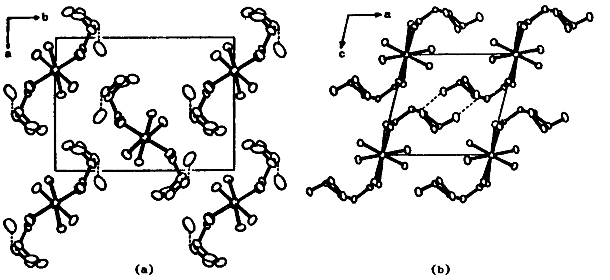


Fig. 2. The projection of (a) $CdCl_2(Hpro)\cdot H_2O$ along the c axis and (b) $CdCl_2(Hhpro)$ along the b axis. (----: Hydrogen bonding)

screens are bundled only by van der Waals' contacts.

The infrared spectra of the free ligand, the deuterated ligand, $CdCl_2(Hpro)\cdot H_2O$, and the deuterated complex are shown in Fig. 3. The deuterated compounds were obtained by recrystallization from 99.75% D_2O. It was already confirmed that the free ligand is a zwitter ion.[6] According to Herlinger and Long,[7] the peaks at 3050 and 1555 cm^{-1} are assigned to NH stretching vibration and NH_2^+ scissors vibration, respectively. The antisymmetric and symmetric stretching vibrations of COO^- are observed at 1619 and 1402 cm^{-1}, respectively. In $CdCl_2(Hpro)\cdot H_2O$, the peak at 3550 cm^{-1} is assigned to the OH stretching vibration of H_2O. Although there is a peak at 3180 cm^{-1} corresponding to the NH stretching vibration, the peak of NH_2^+ scissors vibration can not be assigned because it overlaps with the peaks of H_2O bending and COO^- antisymmetric stretching vibrations. To discuss the carboxyl stretching vibrations, the deuteration of NH_2^+ and H_2O is required since the peak near 1600 cm^{-1} (COO^- antisymmetric stretching) is probably coupled to NH_2^+ modes in Hpro;[7] there are also overlapping NH_2^+ bending and H_2O scissors vibrations[8,9] in $CdCl_2(Hpro)\cdot H_2O$, as mentioned above.

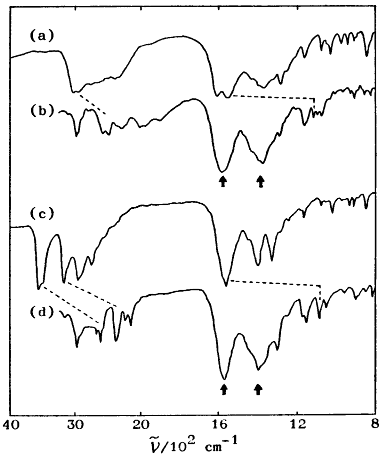
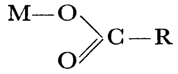
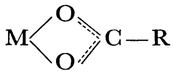
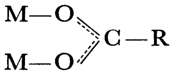


Fig. 3. Infrared spectra of (a) Hpro, (b) the deuterated ligand, (c) $CdCl_2(Hpro)\cdot H_2O$, and (d) the deuterated complex. The shifts of the peaks by deuteration are indicated by the dotted lines. The arrows indicate the peaks of COO^- antisymmetric (left) and symmetric (right) stretching vibrations.

The carboxylate ion may coordinate to a metal in one of the following modes:


(I)


(II)


(III)

In the unidentate complex (structure (I)), the separation between COO^- anti- and symmetric stretching vibrations is much larger than that of the free ion, while it is smaller than that of the free ion in structure (II). In the bridging complex (structure (III)), however, two COO^- stretching vibrations are close to the free ion values.[10] In the present case, this separation evaluated from the deuteration spectrum is 180 cm^{-1}, and the separation for the free ligand is 185 cm^{-1}. This accords with the trend in the structure (III). The trend is also observed in $CdCl_2(Hhpro)$. Thus the trends in the carboxylate ion are likely to be observed in the amino acids which have a pyrrolidine ring.

The results of the simultaneous TG and DTA of $CdCl_2(Hpro)\cdot H_2O$ and of $CdCl_2(Hhpro)$ are shown in Fig. 4. In the former, an endothermic peak on the DTA with a mass loss corresponding to one water molecule is observed at about 80 °C. At about 180 and 210 °C, endothermic peaks on the DTA without mass loss are observed. The complex seems to become an amorphous state; this was confirmed from the X-ray powder pattern. It then melts at 210 °C. At about 230 °C the ligand is thought to decompose and the complex changes into cadmium chloride. About 35% mass loss occurs in the region 230—300 °C. Moreover, from 410 °C about 60% mass loss begins and becomes constant at about 800 °C, where no residue is obtained. Therefore in the region cadmium chloride changes into cadmium oxide and then it is sublimed.[11] The observation of an endothermic peak at 560 °C may indicate that cadmium chloride melts.[12]

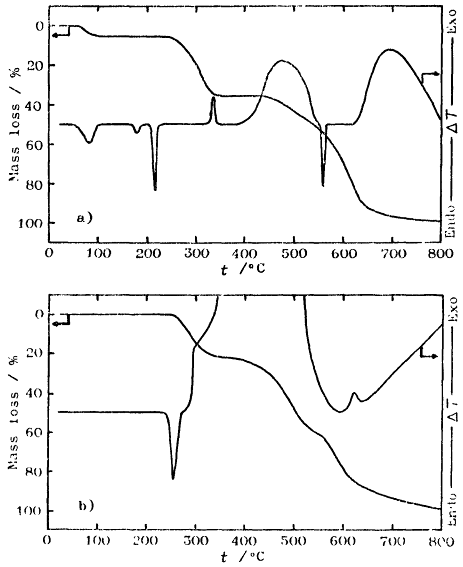


Fig. 4. Thermogravimetric and differential thermal analysis curves of a) $CdCl_2(Hpro)\cdot H_2O$ and b) $CdCl_2$-(Hhpro).

This thermal behavior is not observed in $CdCl_2$-(Hhpro); the DTA curve shows only an endothermic peak at about 210 °C and the complex burns with a gradual mass loss. This difference of the behavior between $CdCl_2$(Hhpro) and $CdCl_2(Hpro)\cdot H_2O$ is thought to be due to the difference of the crystal structure, whether it contains intermolecular hydrogen bonds which connect with the neighboring zigzag folding screen or not.

The authors wish to express their thanks to Professor Yoichi Iitaka for the X-ray diffractometer measurements, and to Dr. Shoichi Sato and Dr. Shin-ichi Nishikiori, The University of Tokyo, for 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. 57430011 from the Ministry of Education, Science and Culture.

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