Preparation and Characterization of Cadmium(II) Halide Complexes with *N*-Substituted Glycines, and the Crystal Structures of Dichloro(*N*-methylglycine)cadmium(II) and Diaquadichloro(*N*,*N*-dimethylglycine)cadmium(II)

Junichi YAMADA, Haruki HASHIMOTO, Yoshie INOMATA,* and Toshio TAKEUCHI
Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102

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Eight cadmium(II) halide complexes with *N*-methylglycine (sarcosine, Hsar), *N*,*N*-dimethylglycine (Hdmgly), and *N*,*N*,*N*-trimethylglycine (betaine, Hbet) have been prepared and characterized by using their infrared absorption spectra and thermal analyses. In addition, the crystal and molecular structures of $[CdCl_2(Hsar)]$ (**1**) and $[CdCl_2(Hdmgly)(H_2O)_2]$ (**2**) were determined by a single-crystal X-ray diffraction method. The crystal data for these two complexes are as follows: Complex (**1**): monoclinic, space group $P2_1/n$, $a=7.960(2)$, $b=13.844(1)$, $c=6.917(1)$ Å, $\beta=92.42(2)°$, $Z=4$. Complex (**2**): monoclinic, space group $P2_1/a$, $a=7.696(2)$, $b=21.854(4)$, $c=6.253(2)$ Å, $\beta=103.69(2)°$, $Z=4$. These structures were solved by the heavy-atom method and refined by full-matrix least-square methods to final R values of 0.043 for 2533 reflections about **1** and 0.068 for 3615 reflections about **2**, respectively. For **1** the structure consists of a one-dimensional polymer bridged by two chlorine atoms. The cadmium atom is hexa-coordinated, being ligated with two oxygen atoms of a carboxyl group and four chlorine atoms. For **2** the cadmium atom is in a distorted octahedral geometry, ligated by a carboxylato oxygen atom, two water molecules, and three chlorine atoms, in which one is terminal and the other two are bridging cadmium atoms to make a polymer.

N-Protected amino acid complexes are of special interest regarding the coordination behavior of a nitrogen atom and carboxylato oxygen atoms as follows.

Cameron et al. reported that in aquabis(*N*,*N*-dimethylglycinato)copper(II) a nitrogen atom and a carboxylato oxygen atom of a ligand were coordinated with a copper atom.[1] In chloro(*N*,*N*-diethylglycinato)copper(II) a nitrogen atom and two carboxylato oxygen atoms of a ligand were coordinated with a copper atom.[2] We previously reported the structures of dichloro(4-hydroxy-L-proline)cadmium(II)[3] and dichloro(L-proline)cadmium(II) hydrate.[4] Both complexes have the structure of a one-dimensional polymer bridged by chlorine atoms and carboxylato oxygen atoms, which are coordinated in a fork-like manner to two cadmium atoms; however, since a nitrogen atom is not coordinated with a cadmium atom, and infinite folding-screen structure is formed.

Chen and Mak reported on the structures of catena-μ-dichloro(betaine)cadmium(II) and dimeric diaquabis(betaine)tetrachlorodicadmium(II);[5] the former has the same structure as that of dichloro(4-hydroxy-L-proline)cadmium(II), and the latter is a dimer with each cadmium atom in a distorted octahedral coordination environment, being surrounded by a chelating bidentate carboxyl group, one water molecule, two bridging chlorine atoms, and one terminal chlorine atom.

Cadmium(II) halide complexes tend to have chloro-bridged structures; catena-μ-dichlorobis(imidazole)cadmium(II)[6] has a linear chain structure, and μ-dichloro(imidazole)cadmium(II)[7] has a double-ribbon structure.

It has been reported that in dichlorobis(glycine)cadmium(II) the cadmium atom is coordinated octahedrally with three chlorine atoms and three oxygen atoms from glycines.[8] Thus, cadmium(II) halide complexes are especially interesting regarding their coordination behavior.

Therefore, in this work we prepared cadmium(II) halide complexes with *N*-methylglycine, *N*,*N*-dimethylglycine, and *N*,*N*,*N*-trimethylglycine; the crystal structures of $[CdCl_2(Hsar)]$ and $[CdCl_2(Hdmgly)(H_2O)_2]$ were determined by means of a single-crystal X-ray diffraction method. These results were compared with those of $[CdCl_2(Hbet)]_2$ and $[CdCl_2(Hbet)(H_2O)]$ analyzed by Chen and Mak.[5]

Experimental

Preparation of Complexes. $[CdCl_2(Hsar)]$, $[CdCl_2(Hdmgly)]$, $[CdCl_2(Hdmgly)(H_2O)_2]$, and $[CdCl_2(Hbet)(H_2O)]$: An aqueous solution containing equimolar amounts of the corresponding *N*-substituted amino acids and $CdCl_2\cdot 2.5H_2O$ was stirred and condensed at about 60 °C in a water bath. This solution was kept at room temperature for $[CdCl_2(Hsar)]$, $[CdCl_2(Hdmgly)]$, and $[CdCl_2(Hbet)(H_2O)]$, while for $[CdCl_2(Hdmgly)(H_2O)_2]$ it was kept in ethanol vapor at room temperature. Clear colorless crystals were obtained from this solution.

$[CdCl_2(Hbet)]$: The complex was prepared by mixing 0.01 mol $CdCl_2\cdot 2.5H_2O$ and 0.01 mol betaine in ethanol.

$[CdBr_2(HL)]$: These complexes were prepared from $CdBr_2\cdot 4H_2O$ and the corresponding *N*-substituted amino acids by the same method as that used for the $[CdCl_2(Hsar)]$ complex.

Deuteration of the Compounds. The deuteration of *N*-methylglycine and *N*,*N*-dimethylglycine as well as their metal complexes was prepared by dissolving these amino acids and each complex in 99.75 atom% D_2O and drying them in a vacuum. NH_2^+ and NH^+ groups were deuterated by this method.

Infrared Absorption Spectra. The infrared absorption spectra from 4000 to 400 cm^{-1} were measured using a JASCO spectrophotometer (Type IR-810). Samples were prepared as KBr disks and Nujol mulls.

Thermal Analysis. Simultaneous TG-DTA measurements were carried out using a Rigaku Denki Thermoflex (M-8075) and a TAS-200 TG 8110D using a sample weighing about 10 mg in each operation. The heating rate was 5 °C min^{-1} in air; α-alumina was used as the reference.

Single-Crystal X-Ray Analysis. The reflections of [CdCl$_2$(Hsar)] and [CdCl$_2$(Hdmgly)(H$_2$O)$_2$] crystals were collected within the $0° < 2\theta < 70°$ range on a Rigaku (AFC-5) automated four-circle X-ray diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71068$ Å), employing the ω–2θ scan technique for [CdCl$_2$(Hsar)] and the ω scan technique for [CdCl$_2$(Hdmgly)(H$_2$O)$_2$]. The cell dimensions of two crystals were obtained by using the respective 25 reflections ($20° < 2\theta < 30°$). Although the 2533 and 3615 reflections for [CdCl$_2$(Hsar)] and [CdCl$_2$(Hdmgly)(H$_2$O)$_2$], respectively, with intensities ($|F_o| > 2.5\sigma(|F_o|)$) were corrected for Lorenz and polarization factors, no corrections were made for the absorption and extinction, because of the low magnitude of μ_r (<1.0). All of the calculations were carried out on HITAC (M680H and M682H) computers at the Computer Center of the University of Tokyo, using UNICS III[9] and ORTEP.[10] The scattering factors were taken from the tables.[11]

The structures were solved by the heavy-atom method. In each case the positions of the cadmium atom and the chlorine atoms were obtained from a Patterson function, while the positions of all the other non-hydrogen atoms were successively located by Fourier syntheses and were refined by a block-diagonal least-squares method. All of the positions of the hydrogen atoms were obtained by difference-Fourier syntheses. In the last cycle by a full-matrix least-squares method with anisotropic temperature factors for all of the non-hydrogen atoms, all of the parameter shifts were less than one-third of the corresponding standard deviations. The weighting scheme was $W = 1/|\Delta F|^2$, $|\Delta F_o|^2 = a|F_o|^2 + b|F_o| + c$. These coefficients were automatically computed in the program system. The final R values were 0.043 for [CdCl$_2$(Hsar)] and 0.068 for [CdCl$_2$(Hdmgly)(H$_2$O)$_2$].

Results and Discussion

The results of elemental analyses are summarized in Table 1. From these results and the IR spectra it is clear that in these complexes Hsar, Hdmgly, and Hbet have zwitter ion structures.

Table 1. Elemental Analyses

Complex[a)]	C/%[b)]	H/%[b)]	N/%[b)]
1 [CdCl$_2$(Hsar)]	13.06	2.47	5.22
	(13.22)	(2.59)	(5.14)
2 [CdBr$_2$(Hsar)]	9.88	1.85	3.89
	(9.97)	(1.95)	(3.88)
3 [CdCl$_2$(Hdmgly)(H$_2$O)$_2$]	14.90	4.17	4.44
	(14.90)	(4.06)	(4.34)
4 [CdCl$_2$(Hdmgly)]	16.61	3.09	4.92
	(16.77)	(3.17)	(4.89)
5 [CdBr$_2$(Hdmgly)]	12.67	2.42	3.84
	(12.80)	(2.42)	(3.73)
6 [CdCl$_2$(Hbet)(H$_2$O)]	18.87	3.99	4.55
	(18.85)	(4.11)	(4.39)
7 [CdCl$_2$(Hbet)]	19.75	3.38	4.59
	(19.98)	(3.69)	(4.66)
8 [CdBr$_2$(Hbet)]	15.42	2.78	3.69
	(15.42)	(2.85)	(3.60)

a) Hsar = C$_3$H$_7$NO$_2$, Hdmgly = C$_4$H$_9$NO$_2$, Hbet = C$_5$H$_{11}$NO$_2$. b) The values in parentheses are calculated one.

Thermal Analysis. The results of the simultaneous TG and DTA of [CdCl$_2$(Hbet)(H$_2$O)] are shown in Fig. 1. The other complexes show the same thermal behavior as that of [CdCl$_2$(Hbet)(H$_2$O)]. The reaction temperature along with the mass loss obtained from the TG and DTA curves are listed in Table 2. As shown in Fig. 1, all of these complexes melted at about 220—300 °C and then began to decompose to cadmium(II) halides. The percentages of the mass loss are in good agreement with the values calculated by assuming that one molecule of the corresponding ligand was released. Then, cadmium(II) halides changed into cadmium(II) oxides, which were sublimed. Observations of the endothermic peaks from about 530 to 570 °C indicated that cadmium(II) halides melt. The same behavior has been observed for dichloro(L-proline)cadmium(II) hydrate.[4)]

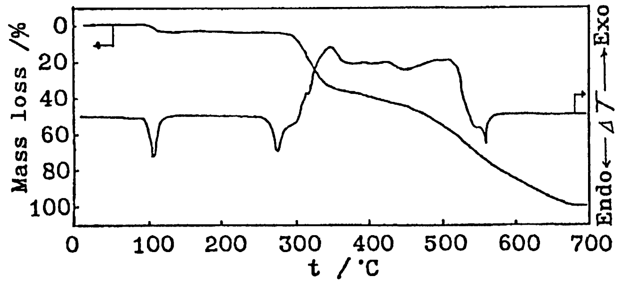

Fig. 1. Thermogravimetric and differential thermal analysis curves of [CdCl$_2$(Hbet)(H$_2$O)].

Infrared Absorption Spectra. The infrared spectral data are listed in Table 3. The assignments were made by referring to *N*-methylglycine,[12)] *N*,*N*-bis(2-hydroxyethyl)glycine,[13)] and *N*,*N*,*N*-trimethylglycine[14)] as well as their metal complexes. The spectra of the bromo complex are similar to those of the corresponding chloro complex over the infrared region.

In [CdCl$_2$(Hsar)], since the bands at 3130, 1600, 1392, and 888 cm^{-1} shifted to 2360, 1333, 1093, and 762 cm^{-1} upon deuteration, respectively, they were tentatively assigned to NH$_2^+$ vibrations (Table 3). As for [CdCl$_2$(Hdmgly)(H$_2$O)$_2$], the band at 3122 cm^{-1}, which sifted to 2264 cm^{-1} upon deuteration, was assigned to the NH$^+$ stretching vibration.

Therefore, the NH$_2^+$ and NH$^+$ groups may be retained in complexes with Hsar and Hdmgly complexes, respectively. From these results, it has been presumed that a nitrogen atom is not coordinated to a cadmium

Table 2. Temperature Range of Decomposition and Mass Loss of Complexes

Complex	Temperature range/°C	Thermal reaction	Mass loss/%	
			Obsd	Calcd
1 [$CdCl_2$(Hsar)]	256—333	endo, exo	31	33[a)]
	432—635	exo, endo		
	(556	melt)		
2 [$CdBr_2$(Hsar)]	253—374	endo, exo	23	25[a)]
	420—580	exo, endo		
	(570	melt)		
3 [$CdCl_2$(Hdmgly)(H_2O)$_2$]	25—148	endo	10	11[b)]
	240—360	endo, exo	44	43[a)]
	550—640	exo, endo		
	(565	melt)		
4 [$CdCl_2$(Hdmgly)]	212—338	endo, exo	33	35[a)]
	501—770	exo, endo		
	(570	melt)		
5 [$CdBr_2$(Hdmgly)]	219—318	endo, exo	26	27[a)]
	426—576	endo		
	(552	melt)		
6 [$CdCl_2$(Hbet)(H_2O)]	103—117	endo	4	5.6[b)]
	287—356	endo, exo	44	43[a)]
	447—700	exo, endo		
	(567	melt)		
7 [$CdCl_2$(Hbet)]	285—375	endo, exo	40	39[a)]
	420—745	exo, endo		
	(560	melt)		
8 [$CdBr_2$(Hbet)]	255—380	endo, exo	33	31[a)]
	425—590	exo, endo		
	(530	melt)		

a) As metal halide. b) As water.

Table 3. Assignments of Infrared Absorption Spectra Related with Metal-Ligand Bonds (cm^{-1})[a)]

Hsar	1	2	Hdmgly	3	4	5	Hbet	6	7	8	Assignments
3030	3130	3120									NH_2^+ str.
			3026	3122	3120	3122					NH^+ str.
1649	1586	1583	1632	1604	1603	1604	1622	1625	1620	1614	COO^- asym. str.
1609	1600	1599									NH_2^+ scissors
1404	1415	1415	1396	1392	1391	1391	1394	1400	1402	1400	COO^- sym. str.
1380	1392	1386									NH_2^+ wagging
895	888	886									NH_2^+ rocking
701	688	692	703	714	714	713	712	740	737	732	COO^- scissors
592	608	609	602	606	606	605	604	604	603	600	COO^- wagging
485	512	506	507	518	519	517	545	551	545	547	COO^- rocking

a) **1** [$CdCl_2$(Hsar)], **2** [$CdBr_2$(Hsar)], **3** [$CdCl_2$(Hdmgly)(H_2O)$_2$], **4** [$CdCl_2$(Hdmgly)], **5** [$CdBr_2$(Hdmgly)], **6** [$CdCl_2$(Hbet)(H_2O)], **7** [$CdCl_2$(Hbet)], **8** [$CdBr_2$(Hbet)].

atom.

The antisymmetric stretching vibrations of the carboxyl group for these metal complexes shift to either lower or higher frequency regions, as compared with those of both ligands. Since the same behavior has also been observed for the symmetric stretching vibrations of the carboxyl group in these metal complexes, carboxylato oxygen atoms are coordinated to cadmium atoms.

Crystal Structure. The crystal data for [$CdCl_2$(Hsar)] and [$CdCl_2$(Hdmgly)(H_2O)$_2$] are given in Table 4. The final atomic parameters are listed in Table 5. The bond lengths and angles are listed in Tables 6 and 7,[15)] respectively. The deviation of atoms from the least-squares planes are shown in Table 8.

Structure of [$CdCl_2$(Hsar)]: The molecular structure of the complex and the numbering scheme of the non-hydrogen atoms are shown in Fig. 2. The crystal structure is shown in Fig. 3. The structure of this complex comprises a one-dimensional polymer chain bridged by chlorine atoms. This polymer chain extends in the direction of the *c*-axis like a twisted zigzag screen. Similar halogen bridged chains have been observed for dibromo(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)cadmium(II)[16)] and dichloro(dimethylphenyl-

Table 4. Crystallographic Data

	[$CdCl_2$(Hsar)]	[$CdCl_2$(Hdmgly)(H_2O)$_2$]
Formula	$CdCl_2C_3H_7NO_2$	$CdCl_2C_4H_{13}NO_4$
Folmula weight	272.41	322.45
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
Z	4	4
a/Å	7.960(2)	7.696(2)
b/Å	13.844(1)	21.854(4)
c/Å	6.917(1)	6.253(2)
β/deg	92.42(2)	103.69(2)
V/Å^3	761.56(1)	1021.9(4)
D_x/g cm^{-3}	2.376	2.096
D_m/g cm^{-3}	2.38(1)	2.09(1)
μ(Mo $K\alpha$)/cm^{-1}	35.0	26.4
R	0.043	0.068
R_w	0.050	0.092
Reflections measured	3226	4393
Reflections used	2533	3615

Table 5. Final Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2) for [$CdCl_2$(Hsar)] and [$CdCl_2$(Hdmgly)(H_2O)$_2$] with the Estimated Standard Deviation in Parentheses

Atom	x	y	z	B_{eq}/B_{iso}
[$CdCl_2$(Hsar)]				
Cd	697(0)	293(0)	2502(0)	1.92
Cl(1)	276(1)	−1248(1)	4413(1)	2.25
Cl(2)	−1912(1)	645(1)	487(1)	2.61
O(1)	2456(4)	1737(2)	2155(5)	2.53
O(2)	3429(4)	471(2)	3772(5)	2.33
N	5619(5)	1530(3)	5965(6)	2.46
C(2)	5003(6)	1919(3)	4073(7)	2.58
C(1)	3517(5)	1340(3)	3261(6)	1.92
C(3)	4430(7)	1626(5)	7527(7)	3.29
[$CdCl_2$(Hdmgly)(H_2O)$_2$]				
Cd	2939(1)	1892(1)	399(1)	1.25
Cl(1)	2563(2)	1041(1)	−2364(3)	2.17
Cl(2)	5000(2)	2535(1)	−1575(2)	1.73
O(1)	5423(6)	1607(2)	3008(8)	1.88
O(2)	4809(7)	620(2)	3376(8)	2.20
OW(1)	3358(6)	2706(2)	3115(8)	1.86
OW(2)	1132(7)	1483(2)	2636(9)	2.35
N	7014(6)	506(2)	7338(8)	1.38
C(1)	5573(6)	1099(2)	4032(9)	1.32
C(2)	6803(8)	1125(2)	6318(9)	1.65
C(3)	8417(9)	148(4)	6637(16)	2.80
C(4)	7334(13)	540(4)	9780(11)	2.89

Table 6. Selected Interatomic Distances (l/Å) with the Estimated Standard Deviations in Parentheses[a]

	[$CdCl_2$(Hsar)]	[$CdCl_2$(Hdmgly)(H_2O)$_2$]
Cd–Cd^{I}	3.680(1)	4.677(1)
Cd–Cl(1)	2.539(1)	2.508(2)
Cd–Cl(2)	2.500(1)	2.636(2)
Cd–Cl(1)^{II}	2.654(1)	—
Cd–Cl(2)^{I}	2.658(1)	—
Cd–Cl(2)^{II}	—	2.624(1)
Cd–O(1)	2.457(3)	2.287(4)
Cd–O(2)	2.324(3)	—
Cd–OW(1)	—	2.429(5)
Cd–OW(2)	—	2.368(6)
O(1)–C(1)	1.243(5)	1.272(7)
O(2)–C(1)	1.257(5)	1.224(7)
C(1)–C(2)	1.516(6)	1.518(7)
C(2)–N	1.480(6)	1.488(7)
C(3)–N	1.472(7)	1.481(10)
C(4)–N	—	1.490(8)
OW(1)···OW(2)^{I}	—	2.844(7)
OW(1)···O(1)^{II}	—	2.700(6)
O(1)···N^{III}	2.912(5)	—
O(2)···N^{III}	—	2.815(6)
O(2)···N^{IV}	2.876(5)	—

a) Key to symmetry operations: [$CdCl_2$(Hsar)]: I $-x$, $-y$, $-z$: II $-x$, $-y$, $1.0-z$: III $x-0.5$, $0.5-y$, $z-0.5$: IV $1.0-x$, $-y$, $1.0-z$. [$CdCl_2$(Hdmgly)(H_2O)$_2$]: I $0.5+x$, $0.5-y$, z: II $-0.5+x$, $0.5-y$, z: III $1.0-x$, $-y$, $1.0-z$: IV x, y, $1.0+z$.

phosphine)cadmium(II).[17]

The cadmium atom is surrounded by the six atoms: two carboxylato oxygen atoms and four chlorine atoms. This complex is in an octahedral geometry, which has a distorted square plane formed by Cl(1), Cl(2), O(1), and O(2). The bond length of Cd–O(1) (2.457(3) Å) is longer than that of Cd–O(2) (2.324(3) Å). Although a similar trend has been observed for [$CdCl_2$(Hbet)(H_2O)] (2.480(2) and 2.332(3) Å),[5] in [$CdCl_2$(Hbet)] the bond lengths of Cd–O are nearly equal to each other (2.329(6) and 2.291(6) Å).[5] [$CdCl_2$(Hhpro)][3] (2.347(3) and 2.303(3) Å about Cd–O) and [$CdCl_2$(Hpro)][4] (2.323(5) and 2.319(5) Å about Cd–O) show the same trend as [$CdCl_2$(Hbet)] concerning the bond lengths of Cd–O.

We now compare the structures of [$CdCl_2$(Hsar)] and [$CdCl_2$(Hbet)(H_2O)] with those of [$CdCl_2$(Hbet)] and [$CdCl_2$(Hhpro)], previously studied in our laboratory.[3] In [$CdCl_2$(Hsar)] two carboxylato oxygen atoms are coordinated to an identical cadmium atom, and a chlorine bridged chain twists as shown in Fig. 2. In [$CdCl_2$(Hbet)(H_2O)], which has a dimeric structure, two carboxylato oxygen atoms behave similarly to those of [$CdCl_2$(Hsar)]. However, in [$CdCl_2$(Hbet)] and [$CdCl_2$(Hhpro)] the cadmium atom is surrounded by four chlorine atoms and two carboxylato oxygen atoms of two molecules of Hbet and Hhpro, respectively, which are coordinated forkedly to two cadmium atoms from the trough position in the zigzag structure. [$CdCl_2$(Hpro)] has the same structure as that of [$CdCl_2$(Hhpro)].

From the above discussion the following conclusion is obtained concerning two bond lengths of Cd–O in [$CdCl_2$(HL)(H_2O)$_n$]-type complexes: When two car-

Table 7. Selected Bond Angles (ϕ/°) with the Estimated Standard Deviations in Parentheses[a)]

	[$CdCl_2$(Hsar)]	[$CdCl_2$(Hdmgly)(H_2O)$_2$]
Cd–Cl(2)–Cd^I	90.97(4)	125.6(1)
Cl(1)–Cd–Cl(2)	109.24(4)	93.3(1)
Cl(1)–Cd–Cl(2)^I	93.15(4)	—
Cl(2)–Cd–Cl(2)^I	89.03(4)	—
Cl(1)–Cd–O(1)	145.32(8)	103.3(1)
Cl(2)–Cd–O(1)	104.46(8)	89.1(1)
Cl(1)–Cd–O(2)	91.96(8)	—
Cl(2)–Cd–O(2)	158.78(8)	—
Cl(1)–Cd–OW(1)	—	178.9(1)
Cl(1)–Cd–OW(2)	—	98.0(1)
Cl(2)–Cd–OW(1)	—	86.6(1)
Cl(2)–Cd–OW(2)	—	168.7(1)
Cl(1)–Cd–C(1)	118.43(8)	—
Cl(2)–Cd–C(1)	131.79(9)	—
O(1)–Cd–O(2)	54.8(1)	—
O(1)–Cd–OW(1)	—	75.6(2)
O(1)–Cd–OW(2)	—	89.1(2)
O(1)–C(1)–O(2)	123.5(4)	126.8(5)
O(1)–C(1)–C(2)	119.6(4)	113.8(4)
O(2)–C(1)–C(2)	116.9(4)	119.4(5)
C(1)–C(2)–N	111.1(4)	110.5(4)
C(2)–N–C(3)	114.7(4)	111.5(5)
C(2)–N–C(4)	—	111.6(5)
C(3)–N–C(4)	—	112.0(6)

a) Key to symmetry operations: [$CdCl_2$(Hsar)]: I $-x$, $-y$, $-z$. [$CdCl_2$(Hdmgly)(H_2O)$_2$]: I $0.5+x$, $0.5-y$, z.

Table 8. Least-Squares Planes and the Deviations of Atom (l/Å)

	[$CdCl_2$(Hsar)]
Plane(1)	[Cd, Cl(1), Cl(2), O(1), O(2), C(1)]
	$0.42250X-0.47465Y-0.77215Z+1.39715=0.0$
	Cd, 0.0734; Cl(1), −0.0989; Cl(2), 0.0643; O(1), −0.0950; O(2), 0.1814; C(1), −0.0814
Plane(2)	[Cd, O(1), O(2), C(1), C(2)]
	$0.46255X-0.32911Y-0.82324Z+1.25689=0.0$
	Cd, −0.0770; O(1), 0.1142; O(2), 0.1077; C(1), 0.0415; C(2), −0.1477
	[$CdCl_2$(Hdmgly)(H_2O)$_2$]
Plane(1)	[Cl(1), Cl(2), OW(1), OW(2)]
	$0.68960X-0.46849Y+0.55224Z+0.28468=0.0$
	Cd, 0.0002; Cl(1), 0.0271; Cl(2), −0.0252; OW(1), 0.0230; OW(2), −0.0178
Plane(2)	[Cd, Cl(1), Cl(2), OW(1), OW(2)]
	$0.68960X-0.46849Y+0.55224Z+0.28464=0.0$
	Cd, 0.0001; Cl(1), 0.0271; Cl(2), −0.0253; OW(1), 0.0229; OW(2), −0.0179

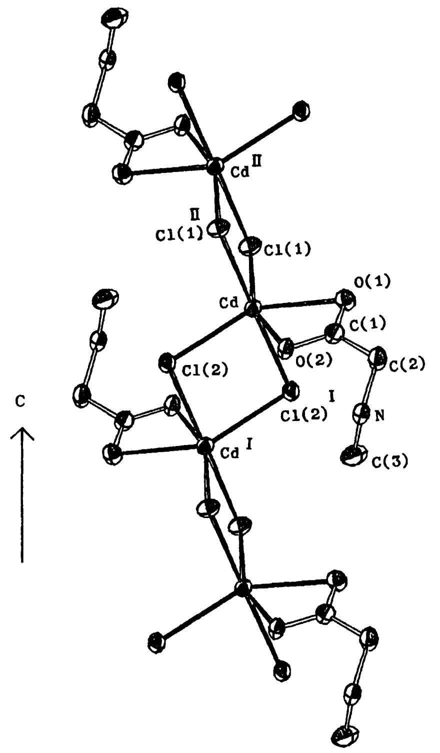

Fig. 2. The perspective drawing of [$CdCl_2$(Hsar)] and the numbering scheme of non-hydrogen atoms. Key to symmetry operations: I $-x$, $-y$, $-z$: II $-x$, $-y$, $1.0-z$.

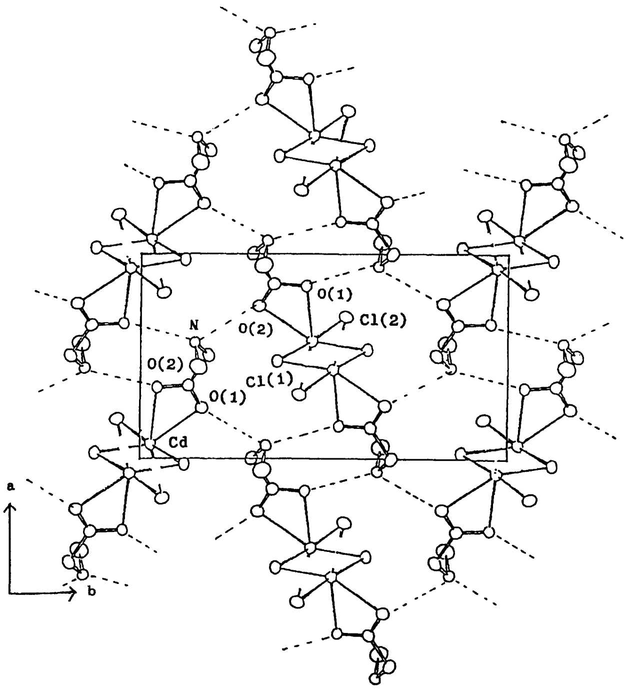

Fig. 3. The projection of [$CdCl_2$(Hsar)] along the c axis. (----: Hydrogen bonding).

boxylato oxygen atoms are coordinated to an identical cadmium atom, the bond lengths of Cd–O are different from each other; when two carboxylato oxygen atoms are coordinated to different cadmium atoms, the bond lengths of Cd–O are nearly equal to each other.

Two hydrogen bonds are found between O(1) and N of the neighboring molecule and between O(2) and N of the other neighboring molecule, as shown in Fig. 3.

Structure of [$CdCl_2$(Hdmgly)(H_2O)$_2$]: The crystal structure of the complex and the numbering scheme of the non-hydrogen atoms are shown in Fig. 4.

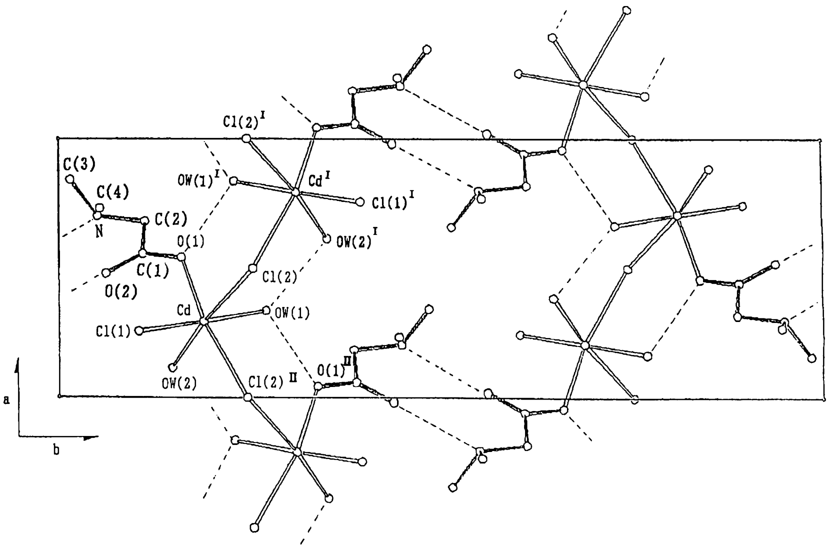

Fig. 4. The projection of $[CdCl_2(Hdmgly)(H_2O)_2]$ along the *c* axis and the numbering scheme of non-hydrogen atoms. (----: Hydrogen bonding). Key to symmetry operation: II $-0.5+x$, $0.5-y$, z.

The cadmium atom is surrounded by six atoms: one carboxylato oxygen atom (O(1)), two chlorine atoms (Cl(1) and Cl(2)), two oxygen atoms of two water molecules, and the chlorine atom of the neighboring unit. The nitrogen atom is not coordinated to a cadmium atom. The structure consists of a one-dimensional polymer chain bridged by a chlorine atom, which is parallel to the *a*-axis, as shown in Fig. 4. While the bond lengths of C(1)–O(1) (1.243(5) Å and C(1)–O(2) (1.257(5) Å) are approximately equal to each other for $[CdCl_2(Hsar)]$, as for $[CdCl_2(Hdmgly)(H_2O)_2]$ these bond lengths (C(1)–O(1) 1.272(7) Å and C(1)–O(2) 1.224(7) Å) are different from each other. This is because in $[CdCl_2(Hsar)]$ the carboxyl group acts as a bidentate ligand, while in $[CdCl_2(Hdmgly)(H_2O)_2]$ this group acts as a monodentate ligand. The same type behavior was reported for $[Cu(dmgly)_2(H_2O)]$ (C(1)–O(1) 1.30(3) Å and C(1)–O(2) 1.21(3) Å), in which the carboxyl group acts as a monodentate.[1] Therefore, the difference between the C–O bond lengths in $[CdCl_2(Hdmgly)(H_2O)_2]$ is due to the difference between a single bond and a double bond.

The cadmium atom is almost on the least-squares plane formed by Cl(1), Cl(2), OW(1), and OW(2). The deviation is only 0.0002 Å. As shown in Fig. 4, three kinds of hydrogen bonds are observed in a lattice.

A comparison of the structure of $[CdCl_2(Hsar)]$ with those of $[CdCl_2(Hbet)]$, $[CdCl_2(Hhpro)]$, and $[CdCl_2(Hpro)]$ has led to the following conclusion about $[CdCl_2(HL)]$-type complexes (HL: amino acids or *N*-substituted amino acids): In the case of a small *N*-substituted group, carboxylato oxygen atoms are coordinated to an identical cadmium atom and chloro bridged polymer chains extend like a twisted zigzag-type screen, while in the case of a bulky *N*-substituted group the carboxylato oxygen atoms are coordinated to different cadmium atoms in a fork-like manner and chloro bridged chains extend in a zigzag manner like an infinite folding screen.

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