Synthetic, Spectroscopic and X-Ray Crystallographic Studies of Bivalent Metal Complexes with Amino Acids Having a Thiazolidine Ring. III. The Properties of Bivalent Metal Complexes with Racemic 2-Thiazolidinecarboxylic Acid and the Structure of *trans*-Diaquabis-(2-thiazolidinecarboxylato)zinc(II)

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Several complexes with the formula of $ML_2 \cdot 2H_2O$ (HL=racemic 2-thiazolidinecarboxylic acid, S-CH_2-CH_2-NH-CH-COOH, M=Co, Ni, Zn), anhydrous CdL_2 and $CdCl_2(HL)$ were synthesized and characterized by means of their infrared absorption and reflection spectra, magnetic susceptibility, thermal analyses, and powder X-ray patterns. In addition, the crystal structure of $ZnL_2 \cdot 2H_2O$ was also determined. Crystals of this complex are monoclinic, with the space group $P2_1/n$ with a=7.224(1), b=18.246(4), c=5.306(1) Å, and β=104.57(1)° and Z=2. The structure was solved by the heavy atom technique and refined by a block-diagonal least-squares method to a final R value of 0.056 for 1774 unique reflections. The zinc environment consists of two carboxylic oxygen atoms and two thiazolidine nitrogen atoms from two centrosymmetrically related organic ligands in a square-planar arrangement. Two water molecules in the axial positions complete a tetragonal bipyramidal coordination around the metal atom. No sulfur atom is coordinated to the zinc atom. The infrared absorption spectra and the structure of this zinc(II) complex are discussed in comparison with those of zinc(II) complexes with (*S*)-4-thiazolidinecarboxylic acid and racemic 4-thiazolidinecarboxylic acid.

As 4-thiazolidinecarboxylic acid has been reported to induce the restoration of the contact inhibition of tumor cells.[1-3] Tatarowski et al.[4] investigated the NMR and crystallography of zinc(II) complexes with 4-thiazolidinecarboxylic acid and 2-thiazolidinecarboxylic acid. Then we ourselves investigated in detail the coordination behavior of racemic and (*S*)-4-thiazolidinecarboxylic acid toward bivalent metals in the solid state.[5,6] These studies have clearly demonstrated that whether or not the nitrogen atom of the thiazolidine ring coordinates to metal ions depends on the pH of the solution used in the preparation. For complexes which have been prepared in a basic aqueous solution, both a carboxylato oxygen atom and the nitrogen atom bind to metal ions.

In the zinc(II) complex with (*S*)-4-thiazolidinecarboxylic acid prepared at pH<7, the zinc atom is ligated with a carboxylato oxygen atom of a (*S*)-thiazolidinium-4-carboxylate, which has a zwitter ion structure, with two carboxylato oxygen atoms, and with the nitrogen atom of a (*S*)-4-thiazolidinecarboxylate anion and a chlorine atom;[5] in dichlorobis(thiazolidinium-4-carboxylate)zinc(II), the zinc atom seems to be ligated through two chlorine atoms and the carboxylato oxygen atom of the racemic thiazolidinium-4-carboxylate, which has a zwitter ion structure.[6]

In order to discuss the effect of the position of the carboxyl group in thiazolidinecarboxylic acid on the structures of complexes, we have now synthesized it by two methods and characterized bivalent metal complexes with racemic 2-thiazolidinecarboxylic acid. The structure of *trans*-diaquabis(2-thiazolidinecarboxylato)zinc(II) has also been determined. Moreover, we have summarized the coordination behavior of metal complexes with (*S*)-4-thiazolidinecarboxylic and racemic acid as well as with racemic 2-thiazolidinecarboxylic acid.

Experimental

Preparation of Racemic 2-Thiazolidinecarboxylic Acid.[7] An ethanol solution (59.2 g) containing 25% of glyoxylic acid was slowly added to 200 cm^3 of an ethanol solution including 35.5 g (0.31 mol) of cysteamine hydrochloride. This mixed solution was then refluxed for 90 minutes at 80 °C. After the solution had then cooled until room temperature, colorless crystals were precipitated. After these crystals had been separated, they were recrystallized from water and dried in a silica-gel desiccator.

Preparation of Complexes. $CoL_2 \cdot 2H_2O$ was prepared by adding 0.01 mol of fresh cobalt(II) hydroxide to a hot aqueous solution containing 0.02 mol of racemic 2-thiazolidinecarboxylic acid. After the solution had been stirred for an hour in a water bath at 60 °C, the precipitate which formed was filtered, washed with water, and dried in vacuo for six hours at room temperature. $NiL_2 \cdot 2H_2O$, $ZnL_2 \cdot 2H_2O$, and CdL_2 were prepared from the corresponding metal hydroxides by the same procedure as was used for the cobalt(II) complex. The crystal used for the single crystal X-ray analysis was prepared by keeping the saturated aqueous solution for two weeks at room temperature.

$CdCl_2(HL)$ was prepared by adding 0.01 mol of cadmium-

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(II) chloride to an aqueous solution containing 0.01 mol of this ligand. The mixed solution, after it had been stirred and condensed for an hour at 80 °C, was allowed to stand for two weeks. The crystals thus precipitated were dried in vacuo for six hours at room temperature.

Deuterated complexes were obtained by recrystallization in D_2O.

Physical Measurements. The powder diffuse reflection and infrared absorption spectra, magnetic moments, and thermal analysis were obtained by the methods described in previous papers.[5,6]

Single Crystal X-Ray Analysis. The reflection intensities were collected by the ω-2θ scan technique on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo$K\alpha$ radiation. 1774 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the refinement. The intensities were corrected for the Lorentz and polarization factors: however, no corrections were made for absorption and extinction because $\mu r(<1)$.

All the calculations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo, using the local version of UNICS.[8] The scattering factors were taken from the tables.[9]

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. The positions of the zinc and oxygen atoms were obtained from a three-dimensional Patterson map, while the positions of all the other non-hydrogen atoms were successively located by Fourier syntheses. The positions of the hydrogen atoms were obtained by means of difference-Fourier syntheses. The weighting scheme was $w=1/[\{\sigma(|F_o|)\}^2+(0.02\times|F_o|)^2]$. 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 0.056.

Results and Discussion

The results obtained from the elemental analyses and those of the reflection spectra and magnetic moment calculations are listed in Tables 1 and 2 respectively. These results and the infrared spectra suggest that there are two types of complexes: A and B. The A type is $ML_2\cdot nH_2O$ (M=Co(II), Ni(II), Zn(II), Cd(II), HL=racemic 2-thiazolidinecarboxylic acid n=0, 2). The B type is $CdCl_2$(HL).

The reflection spectra and magnetic moments are similar to those of the corresponding complexes with racemic 4-thiazolidinecarboxylic acid. From these

Table 1. Elemental Analyses of Racemic 2-Thiazolidinecarboxylic Acid (HL) and Its Metal Complexes

Compound	Found (Calcd) /%				
	H	C	N	M	Cl
HL	5.54 (5.30)	35.45 (36.07)	10.52 (10.52)		
$CoL_2\cdot 2H_2O$	4.25 (4.49)	26.93 (26.74)	7.65 (7.80)	16.4 (16.40)	
$NiL_2\cdot 2H_2O$	4.57 (4.49)	27.03 (26.76)	7.87 (7.80)	16.5 (16.35)	
$ZnL_2\cdot 2H_2O$	4.43 (4.41)	26.20 (26.27)	7.48 (7.66)	17.8 (17.88)	
CdL_2	3.24 (3.21)	25.29 (25.50)	7.32 (7.44)	29.1 (29.84)	
$CdCl_2$(HL)	2.38 (2.23)	14.79 (15.18)	4.18 (4.43)	35.6 (35.52)	22.40 (21.67)

Table 2. Magnetic Moments and Powder Diffuse Reflection Spectra of Metal Complexes with Racemic 2-Thiazolidinecarboxylic Acid

	Co(II)	Ni(II)
Magnetic moment μ_{eff}/BM	4.67 (3.87)[a]	3.34 (2.83)[a]
Reflection spectra λ/nm	1050 ($^4T_{2g}\leftarrow{}^4T_{1g}$)	920 ($^3T_{2g}\leftarrow{}^3A_{2g}$)
	535 ($^4A_{2g}\leftarrow{}^4T_{1g}$)	626 ($^3T_{1g}\leftarrow{}^3A_{2g}$)
	450 ($^4T_{1g}(P)\leftarrow{}^4T_{1g}$)	385 ($^1A_{1g}\leftarrow{}^3A_{2g}$)
		356 ($^3T_{1g}(P)\leftarrow{}^3A_{2g}$)

a) Spin-only value.

Table 3. Temperature Range of Decomposition and Mass Loss of Racemic 2-Thiazolidinecarboxylic Acid Complexes

Complex	Temperature range/°C	Thermal reaction	Mass loss/% Observed	Calculated
$CoL_2\cdot 2H_2O$	141—195	Endo	10.7	10.0
	216—426	Exo		
	435—525	Exo	78.6	79.1[a]
$NiL_2\cdot 2H_2O$	159—219	Endo	10.8	10.0
	219—438	Exo		
	447—549	Exo	73.1	79.2[a]
$ZnL_2\cdot 2H_2O$	117—177	Endo	9.4	9.8
	252—516	Exo		
	555—666	Exo	77.1	77.5[a]
CdL_2	249—459	Exo	59.0	61.7[b]
	745—	Exo		65.9[a]
$CdCl_2$(HL)	190		Melt	
	190—265	Exo		
	470—720	Exo		
	790—920	Exo	Sublimated	

a) As metal oxide. b) As metal sulfide.

assignments of the reflection spectra, it seems that the cobalt(II) and nickel(II) complexes have an octahedral configuration, as is suggested by reference to the X-ray analyses for diaqua((*S*)-4-thiazolidinecarboxylato)-zinc(II)[4] and diaqua(2-thiazolidinecarboxylato)-zinc(II) to be discussed below and by the reflection spectra of other complexes.[10-12]

Thermal Analysis. The temperature range and the percentage of the mass loss obtained from the TG and DTA curves are summarized in Table 3. The cobalt(II), nickel(II), and zinc(II) complexes release two molecules of water in the first endothermic reaction. Thereafter these complexes change to the corresponding metal oxides in an exothermic reaction.

The cadmium(II)-A complex gives two exothermic reaction steps with a mass loss. In the first step, the cadmium(II)-A complex becomes cadmium sulfide; then this sulfide seems to change to cadmium oxide in the second step.

For the cadmium(II)-B complex, an endothermic peak is observed at about 190 °C. This peak is assigned to the melt of this complex. After that, the exothermic reaction occurs immediately, with a mass loss, and the complex decomposes to cadmium halide. Finally, after several exothermic reactions with a gradual mass loss, no residual is obtained. In these steps, cadmium halide changes into cadmium oxide, which then sublimes. The same behavior is observed for dichloro(4-hydroxy-L-proline)cadmium(II).[13]

Infrared Absorption Spectra. The infrared spectral data are listed in Table 4. The assignments of the observed frequencies have been made by referring to (*S*)-4-thiazolidinecarboxylic acid, racemic 4-thiazolidinecarboxylic acid, and their metal complexes.[5,6] In the zinc(II) complex, the absorption bands are assigned through comparison with its deuterated compound.

Racemic 2-Thiazolidinecarboxylic Acid: Some bands shift to a lower frequency region on deuteration. They are assigned to the NH_2^+ stretching and bending vibrations. The bands at 1610 cm^{-1} and at 1360 cm^{-1} are assigned to the COO^- antisymmetric and symmetric stretching vibrations respectively. Thus, this ligand has a zwitter ion structure.

Complexes: For the zinc(II) complex, some absorption bands which can be observed in the ligand disappear, while new bands which shift to a lower frequency region on deuteration can be observed. These are assigned to the NH stretching and bending vibrations.

The antisymmetric and symmetric stretching vibrations of the carboxyl group shift to higher frequency regions than those of the free ligand. Therefore, in the zinc(II) complex, each zinc atom is coordinated through a carboxylato oxygen atom and a nitrogen atom of the thiazolidine ring. This fact is confirmed by X-ray analysis.

Since, in the A-type complexes, the C-S stretching vibrations are observed in the same region as for the zinc(II) complex, the sulfur atoms do not seem to be associated with coordination.

The spectra of the cadmium(II)-B complex is different from that of the cadmium(II)-A complex. Some absorption bands due to NH_2^+ vibrations are observed in the same region as those of the free ligand. The antisymmetric and symmetric stretching vibrations of the carboxyl group shift to lower and higher frequency regions respectively than those of the free ligand. The frequency separation between the antisymmetric and symmetric stretching vibrations of the carboxyl group (Δ) is smaller than that of the free ligand.

Deacon and Phillips[14] arrived at the following conclusions on the basis of an examination of the infrared absorption spectra of many acetates and trifluoroacetates with known X-ray crystal structures.[15] Unidentate complexes exhibit Δ values much greater than those of ionic complexes. Chelating (bidentate) complexes exhibit Δ values significantly lower than the ionic values. The Δ values for bridging complexes are close to the ionic values. Therefore, in the cadmium(II)-B complex, two oxygen atoms of the carboxyl group seem to be coordinated with the cadmium atom by either bidentate or bridging types. It has been determined by X-ray analysis that dichloro-(4-hydroxy-L-proline)cadmium(II)[13] and dichloro-(L-proline)cadmium(II) hydrate[16] have bridging carboxyl groups and that dichloro(*N*-methylglycine)-cadmium(II)[17] has a bidentate carboxyl group.

Structure of $ZnL_2 \cdot 2H_2O$. The crystal data are

Table 4. Assignments of Infrared Absorption Spectra of Racemic 2-Thiazolidinecarboxylic Acid (HL) and Its Complexes (cm^{-1})

HL	Co(II)	Ni(II)	Zn(II)	Cd(II)-A	Cd(II)-B	Assignments
	3290	3280	3275	3200		NH str.
3035					3180	NH_2^+ srt.
1610	1614	1612	1613	1582	1596	COO^- asym. str.
1429					1430	NH_2^+ scissors
1360	1374	1380	1378	1407	1380	COO^- sym. str.
1315					1320	NH_2^+ wagging
580	569	576	568	566	583	C-S str.

given in Table 5. The final atomic parameters are listed in Table 6.[18] The bond lengths and bond angles are shown in Tables 7 and 8 respectively. A perspective drawing of the complex, together with the numbering scheme of the non-hydrogen atoms, is shown in Fig. 1. The projection of the unit cell along the b axis is shown in Fig. 2. The zinc atom lies on a center of symmetry and is octahedrally trans-coordinated: two nitrogen atoms of two thiazolidine rings, two oxygen atoms of two carboxyl groups, and two oxygen atoms of two water molecules. In diaquabis((*S*)-4-thiazolidinecarboxylato)zinc(II), however, the zinc atom was octahedrally coordinated by two oxygen and two nitrogen atoms of two ligands and two water molecules in the cis position.[4] The bond distance of Zn-O(w) is longer than that of diaquabis(4-thiazolidinecarboxylato)zinc(II), which

Table 5. Crystal Data of $[ZnL_2(H_2O)_2]$

$ZnC_8H_{16}N_2O_6S_2$	
F. W.	365.76
Monoclinic	
$P2_1/n$	
a/Å	7.224(1)
b/Å	18.246(4)
c/Å	5.306(1)
β/°	104.57(1)
V/Å^3	676.9(2)
Z	2
D_m/g cm^{-3}	1.79
D_x/g cm^{-3}	1.80
λ(Mo $K\alpha$)/Å	0.71073
μ/cm^{-1}	21.7

Table 6. Final Positional Parameters ($\times 10^4$) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2),[a] for $[ZnL_2(H_2O)_2]$, with the Estimated Standard Deviations in Parentheses[b]

Atom	x	y	z	B_{eq}/Å^2
Zn	0.0(0)	0.0(0)	0.0(0)	2.13
S	3867.4(21)	−1935.0(7)	680.8(29)	5.34
O(W)	1894(3)	673(1)	3064(5)	2.58
O(1)	1941(3)	−71(1)	−2243(5)	2.64
O(2)	4355(4)	−724(2)	−2850(5)	3.43
N(3)	1531(4)	−920(2)	1834(5)	2.07
C(4)	3299(5)	−970(2)	949(6)	2.31
C(5)	528(6)	−1632(2)	1444(9)	3.62
C(6)	2023(7)	−2222(2)	2192(9)	4.00
C(7)	3197(4)	−561(2)	−1594(6)	2.12

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression:

$$B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha).$$

The B_{ij}'s are defined by:

$$\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+hlB_{13}+hkB_{12})].$$

b) The final atomic parameters of hydrogen atoms have been deposited.[18]

Table 7. Interatomic Distances of $[ZnL_2(H_2O)_2]$, with the Estimated Standard Deviations in Parentheses

Interatomic distance	l/Å	Interatomic distance	l/Å
Zn-O(W)	2.214(2)	S-C(4)	1.822(4)
Zn-O(1)	2.059(3)	S-C(6)	1.797(6)
Zn-N(3)	2.109(3)	N(3)-C(4)	1.470(5)
		N(3)-C(5)	1.475(5)
O(1)-C(7)	1.259(4)	C(4)-C(7)	1.527(5)
O(2)-C(7)	1.230(5)	C(5)-C(6)	1.506(6)

Table 8. Bond Angles of $[ZnL_2(H_2O)_2]$, with the Estimated Standard Deviations in Parentheses

Bond angle	ϕ/°	Bond angle	ϕ/°
O(W)-Zn-O(1)	94.3(1)	S-C(4)-N(3)	108.4(2)
O(W)-Zn-N(3)	87.0(1)	S-C(4)-C(7)	111.4(3)
O(1)-Zn-N(3)	82.1(1)	N(3)-C(4)-C(7)	113.5(3)
C(4)-S-C(6)	92.3(2)	N(3)-C(5)-C(6)	107.3(3)
Zn-O(1)-C(7)	115.8(2)	S-C(6)-C(5)	103.7(3)
Zn-N(3)-C(4)	107.4(2)	O(1)-C(7)-O(2)	124.4(3)
Zn-N(3)-C(5)	117.0(2)	O(1)-C(7)-C(4)	117.4(3)
C(4)-N(3)-C(5)	109.7(3)	O(2)-C(7)-C(4)	118.2(3)

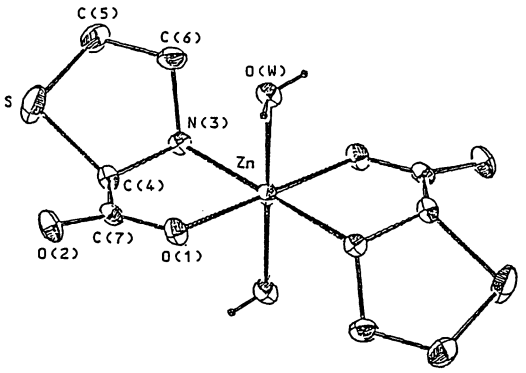

Fig. 1. The perspective drawing of $[ZnL_2(H_2O)_2]$ and the numbering scheme of non-hydrogen atoms.

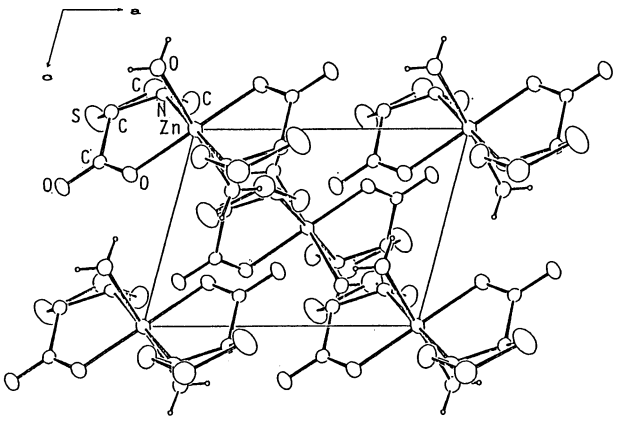

Fig. 2. The molecular packing of $[ZnL_2(H_2O)_2]$ along the b axis.

Table 9. Metal Complexes with Thiazolidinecarboxylic Acids and Coordination Behavior

Type	Metal	(*S*)-4-HL	Racemic-4-HL	Racemic-2-HL
A	Cobalt	CoL_2 (N,O)chelate	$CoL_2 \cdot 2H_2O$ (N,O)chelate	$CoL_2 \cdot 2H_2O$ (N,O)chelate
	Nickel	$NiL_2 \cdot 2H_2O$ (N,O)chelate	$NiL_2 \cdot 2H_2O$ (N,O)chelate	$NiL_2 \cdot 2H_2O$ (N,O)chelate
	Zinc	$ZnL_2 \cdot 2H_2O$ (N,O)chelate	$ZnL_2 \cdot 2H_2O$ (N,O)chelate	$ZnL_2 \cdot 2H_2O$ (N,O)chelate
	Cadmium	CdL_2 (N,O)chelate	CdL_2 (N,O)chelate	CdL_2 (N,O)chelate
B	Zinc	ZnClL(HL) Cl,O,(N,O[a])chelate	$ZnCl_2(HL)_2$ Cl,O	—[b]
	Cadmium	—[b]	—[b]	$CdCl_2(HL)$ Cl,O
		Ref. 5	Ref. 6	This Work

(*S*)-4-HL: (*S*)-4-thiazolidinecarboxylic acid. Racemic-4-HL: racemic 4-thiazolidinecarboxylic acid. Racemic-2-HL: racemic 2-thiazolidinecarboxylic acid. a) Bridging atom. b) Attempts to prepare these complexes in our laboratory were unsuccessful.

was determined by Tatarowski et al.,[4] while the bond distances of Zn-O(1) 2.059(3) and Zn-N(3) 2.109(3) Å are shorter than those of that complex (Zn-O, 2.137(8) and 2.172(8) Å; Zn-N, 2.149(12) and 2.134(12) Å).

The bond angle values of O(1)-Zn-N(3)(82.1(1)°) and O(w)-Zn-O(1)(94.3(1)°) are a little larger than those of diaqua(4-thiazolidinecarboxylato)zinc(II) (78.1(4) and 92.4(4)°). The differences between these and Tatarowski's results are due to the different geometry— that is, cis or trans.

Table 9 summarizes the data for metal complexes with (*S*)-4-thiazolidinecarboxylic acid, racemic 4-thiazolidinecarboxylic acid, and racemic 2-thiazolidinecarboxylic acid, which have been prepared in our laboratory, and the atoms coordinated to the metal atoms.

As for all A-type complexes, the nitrogen atom and an oxygen atom coordinate to the metal ion and form a chelate ring; in some B-type complexes, except for the zinc(II) complex with (*S*)-4-thiazolidinecarboxylic acid, an oxygen atom and chlorine atoms coordinate to the zinc atom. Therefore, in A-type complexes there are no effects of the position of the carboxyl groups in thiazolidinecarboxylic acids on the coordination of the complexes.

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18) The final positional parameters and equivalent isotropic temperature factors of the hydrogen atoms, the final thermal parameters, and the final F_o—F_c table are deposited as Document No. 8895 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.