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Synthetic, Spectroscopic and X-Ray Crystallographic Studies of Bivalent Metal Complexes with Amino Acids Having a Thiazolidine Ring. I. Properties of Bivalent Metal Complexes with (*S*)-4-Thiazolidinecarboxylic Acid and the Structure of Chloro((*S*)-4-thiazolidinecarboxylato)((*S*)-thiazolidinium-4-carboxylate)zinc(II)

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Complexes of five bivalent metals with (*S*)-4-thiazolidinecarboxylic acid($\overline{\mathrm{CH_2{-}S{-}CH_2{-}NH{-}CH}}\mathrm{{-}COOH}$) have been prepared by three methods and characterized by means of infrared absorption, reflection spectra, magnetic susceptibility, thermal analysis, powder X-ray patterns, and single crystal X-ray diffraction. Two types of complexes were found. The first type[A] included $\mathrm{ML_2 \cdot }n\mathrm{H_2O}$ (M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II); L=(*S*)-4-thiazolidinecarboxylate anion) and ZnClL(HL) was the second type[B]. In A-type complexes, the ligand coordinates to the metal with a nitrogen atom and an oxygen atom. From the results of single-crystal X-ray diffraction studies, the second type-B ZnClL(HL) was found to be orthorhombic, with the space group $P2_12_12_1$; a=9.719(2), b=22.194(4), c=5.8537(5) Å, U=1262.6(4) Å^3, Z=4, D_m=1.91 Mg m^{-3}, D_x=1.93 Mg m^{-3}, and μ(Mo $K\alpha$)=25.3 cm^{-1}. Block-diagonal least-squares refinements have led to a final R value of 0.045. The zinc atom is penta-coordinated, being ligated with one carboxylate oxygen atom of (*S*)-thiazolidinium-4-carboxylate, which has a zwitter ion structure, two carboxylato oxygen atoms and one nitrogen atom of (*S*)-4-thiazolidinecarboxylate anion, and a chloride atom. The structure comprises one-dimensional polymers by the carboxylate oxygen atom of this anion-type ligand. The plane extends in the direction of c-axis. In neither the A- nor the B-type complexes does the ligand coordinate to a metal with a sulfur atom.

In our laboratory, we have been investigating the syntheses, spectral properties[1] and crystal structures[2,3] of the metal complexes of various amino acids and their derivatives. This study is one part of that program. (*S*)-4-Thiazolidinecarboxylic acid is a very interesting ligand, since it has four coordination atoms. They are the sulfur and nitrogen atoms of the thiazolidine ring and two oxygen atoms of the carboxyl group.

Recently, this amino acid has been reported to be a new type of anticancer agent which can induce a reverse transformation.[4–7] Thus, many studies have been reported about the stability constants,[8–11] ESR[12] and NMR spectra[13,14] for metal complexes with this ligand in aqueous solution.

The crystal structures of copper(II),[15] zinc(II),[13] and cobalt(III) complexes[16] in the solid state have been reported and their IR spectra discussed.[8]

In the present work, we prepared bivalent metal complexes of (*S*)-4-thiazolidinecarboxylic acid (HL) and systematically investigated their spectral and thermal properties as well as magnetic susceptibilities in the solid state. We then determined the structure of ZnClL(HL) by the single-crystal X-ray diffraction method.

Experimental

Preparation of Compounds. Cobalt(II)-A complex was prepared by adding 0.01 mol cobalt(II) hydroxide to an aqueous solution containing 0.02 mol (*S*)-4-thiazolidinecarboxylic acid. The mixed solution was stirred and concentrated to a small volume in a water bath under 60 °C. The pink precipitate which formed was filtered and washed with water.

Nickel(II)-A, cadmium(II)-A, and zinc(II)-A complexes were prepared by the same method as used for the cobalt(II)-A complex. Zinc(II)-A complex was recrystallized from water.

Copper(II)-A complex was prepared by adding 0.01 mol copper(II) hydroxide to an ethanol solution containing 0.02 mol of this ligand in suspension. This solution was evaporated at room temperature. The resulting complex was recrystallized from methanol.

Zinc(II)-B complex was prepared by adding 0.01 mol of zinc(II) chloride to an aqueous solution containing 0.02 mol of the ligand. The mixed solution was stirred in a water bath, then concentrated to a small volume below 60 °C and filtered. The obtained crude crystals were recrystallized by water under 60 °C. All complexes were dried in vacuo.

Deuterated complexes were obtained by recrystallization in D_2O.

Reflection Spectra. Reflection spectra from 800 to 2000 nm were obtained with a Japan Spectroscopic Co. UVIDEC-590 spectrophotometer. The spectra from 370 to 800 nm were obtained with a Hitachi 624 digital spectrophotometer. Both spectrophotometers were equipped with a standard reflection attachment and a magnesium oxide standard.

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Magnetic Studies. The magnetic moments of these complexes were obtained for the solid samples by the Gouy method, using $Hg[Co(SCN)_4]$ as the calibration standard at 23.5 °C. However, copper(II)-A type complex was measured by the Faraday method.

Infrared and Far Infrared Absorption Spectra. Infrared absorption spectra from 4000 to 400 cm^{-1} were measured using a Hitachi spectrophotometer, type EPI-G_2. Far-infrared absorption spectra from 700 to 200 cm^{-1} were measured using a Hitachi spectrophotometer, type EPI-L. Samples were prepared as KBr disks and Nujol mulls. The spectra were calibrated with polystyrene and atmospheric water vapor.

Thermal Analysis. Simultaneous TG-DTA measurements were carried out with a Rigaku Denki M8075, using a sample weight of about 9 mg in each operation. The heating rate was 10 °C min^{-1}, under static air, using α-alumina as a reference.

Powder X-Ray Diffraction. Powder X-ray diffraction patterns were obtained with a Rigaku RAD IIA powder X-ray diffractometer, using Cu $K\alpha$ radiation over a 2θ range from 50° to 5°.

Single-Crystal X-Ray Analysis. The reflection intensities were collected by the θ–2θ scan technique ($2\theta<70°$) on a Rigaku AFC-6A automated four-circule diffractometer. The intensities were corrected for Lorenz and polarization factors; however, no corrections were made for absorption and extinction $\mu r(=0.51)$. Independent reflections (2378) with $|F_o|>3\sigma(|F_o|)$ were used for a structure determination. All calculations were carried out on a HITAC M-680H computer at the Computer Center of the University of Tokyo, using a local version of UNICS.[17] The scattering factors were taken from Ref. 18.

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. The positions of the zinc and chlorine 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. Since the positions of hydrogen atoms were obtained by difference-Fourier syntheses, all of the positions were calculated and fixed. Their isotropic temperature factors were all assumed to be 3.0 Å^2. 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 values ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0.045.

Results and Discussion

The results of elemental analyses and infrared spectra suggest that there are two types of complexes: A and B types. A type is $ML_2\cdot nH_2O$ (M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II)); HL=(*S*)-4-thiazolidinecarboxylic acid; $n=0$, 2). B type is ZnClL(HL).

Reflection Spectra and Magnetic Moments. The results obtained from elemental analyses, reflection spectra and magnetic moment calculations are listed in Table 1. Each peak of these reflection spectra is due to a d–d transition. The magnetic moment of the cobalt(II)-A complex is within the range expected for high-spin complexes (4.1—5.2 B M for cobalt(II).[19] For nickel(II)-A and copper(II)-A complexes the magnetic moments are within the ranges expected for two unpaired electrons (2.8—4.0 B M for nickel(II)[19]) and for one unpaired electron (1.7—2.2 B M for copper(II)[19]), respectively.

Infrared Absorption Spectra. The infrared spectra data are listed in Table 2. The assignments of observed spectra have been made by referring to L-proline,[20] 4-hydroxy-L-proline[1] and their metal complexes,[1,20] and zinc(II) complex with (*S*)-4-thiazolidinecarboxylic acid.[8]

(*S*)-4-Thiazolidinecarboxylic Acid: X-Ray analyses showed that this amino acid has a zwitter ion structure.[21,22] Therefore, some absorption bands which shift to low-frequency regions on deuteration were assigned to NH_2^+ stretching and bending vibrations. The antisymmetric and symmetric stretching vibrations of the carboxyl group appear at 1625 and 1387 cm^{-1}, respectively.

A Type Complexes: According to the X-ray

Table 1. Analytical Data and Physical Properties

	Complex	Found (Calcd)/%					Magnetic moment μ_{eff}/BM	Reflection spectra λ/nm
		H	C	N	M	Cl		
	CoL_2	3.70	29.19	8.58	17.6	—	4.59	1555, 1160, 543, 500, 467
		(3.74)	(29.72)	(8.67)	(18.23)	(0)		
	$NiL_2\cdot 2H_2O$	4.43	26.13	7.63	16.7	—	3.14	1730, 1010, 752, 640, 478, 389
		(4.49)	(26.76)	(7.80)	(16.35)	(0)		
(A)	CuL_2	3.66	28.92	8.47	19.2	—	1.76	1725, 1560, 655
		(3.69)	(29.30)	(8.55)	(19.38)	(0)		
	$ZnL_2\cdot 2H_2O$	4.35	25.90	7.53	18.0	—	dia	—
		(4.41)	(26.27)	(7.66)	(17.88)	(0)		
	CdL_2	3.19	25.30	7.44	29.7	—	dia	—
		(3.21)	(25.50)	(7.44)	(29.84)	(0)		
(B)	ZnClL(HL)	3.51	26.09	7.60	18.0	9.96	dia	—
		(3.58)	(26.24)	(7.65)	(17.86)	(9.68)		

HL=(*S*)-4-thiazolidinecarboxylic acid.

Table 2. Assignments of Infrared Absorption Spectra Related with Metal–Ligand Bonds ($\mathrm{cm^{-1}}$)[a)]

Ligand	Co(II)-A	Ni(II)-A	Cu(II)-A	Zn(II)-A	Cd(II)-A	Zn(II)-B	Assignment
	3225 s	3195 s	3250 s	3190 s	3265 s	3228 m	NH str.
			3197 sh				
3040 m						3085 m	$\mathrm{NH_2^+}$ str.
						3025 m	
						1683 sh	
						1635 sh	
1625 vs	1609 vs	1599 vs	1637 vs	1603 vs	1592 vs	1624 vs	$\mathrm{COO^-}$ asym. str.
1547 w						1583 sh	$\mathrm{NH_2^+}$ scissors
1463 w						1457 w	$\mathrm{NH_2^+}$ wagging
1387 s	1404 w	1405 s	1362 s	1402 s	1407 s	1403 s	$\mathrm{COO^-}$ sym. str.
862 s						867 m	$\mathrm{NH_2^+}$ rocking
751 m		736 w	748 w	732 w		749 w	$\mathrm{COO^-}$ scissors
623 s	638 w	635 w		627 s	626 w	634 s	C–S str.
	628 w						
592 w	583 sh				593 vw	604 w	$\mathrm{COO^-}$ wagging
462 m		445 b	440 w	445 w	421 w	460 w	$\mathrm{COO^-}$ rocking
	320 m	325 vwb	320 m		324 s	328 m	M–O str.

a) Abbreviations: s=strong; m=medium; w=weak; v=very; sh=shoulder; b=broad.

analysis of Tatarowski et al. diaquabis((*S*)-4-thiazolidinecarboxylato)zinc(II) has an octahedral configuration with the two water molecules occupying cis positions and with nitrogen and oxygen atoms in the ligands.[13)]

Zinc(II)-A complex has a few absorption bands which shift to lower-frequency regions on deuteration. These were assigned to NH stretching and bending vibrations. The antisymmetric stretching vibration of the carboxyl group shifts to a lower-frequency region compared with that of the ligand, and the symmetric stretching vibration shifts to a higher-frequency region. The C–S stretching vibration was observed at the same position as that of the free ligand. Therefore, in this complex, the zinc atom is not coordinated through a sulfur atom, but is coordinated through an oxygen atom of the carboxyl group and a nitrogen atom of the thiazolidine ring; this agrees with Tatarowski's result.[13)]

Bigoli et al. have investigated the structure of *trans*-diaqua((*S*)-4-thiazolidinecarboxylato)((*S*)-4,5-dihydro-4-thiazolecarboxylato)copper(II) by a single-crystal X-ray analysis.[15)] They reported that part of the thiazolidine ligand was oxidized during the reaction. Two different ligands were involved in the complex and the coordination polyhedron around copper(II) atom was a distorted tetragonal bipyramid with the apices of the elongated axis occupied unsymmetrically by water molecules. Since the results of the elemental analyses of copper(II)-A complex show that this complex has two molecules of (*S*)-4-thiazolidinecarboxylate ion for one copper atom, its structure must be different from that of the copper(II) complex which was determined by Bigoli et al.

The absorption bands due to the vibration of the carboxyl and the amino groups for cobalt(II)-A, nickel(II)-A, copper(II)-A, and cadmium(II)-A complexes appear in the same region as those of the zinc(II)-A complex (as shown in Table 2). Therefore, the metal is coordinated through one oxygen and one nitrogen atom for A-type complexes.

From 500 to 200 $\mathrm{cm^{-1}}$, absorption bands which cannot be observed in the ligand appear in cobalt(II)-A, copper(II)-A, cadmium(II)-A, and zinc(II)-B complexes. These are assigned to the M–O stretching vibrations by comparing these spectra with those of metal complexes with L-proline[20)] and 4-hydroxy-L-proline.[1)] For nickel(II)-A and zinc(II)-A complexes, the corresponding bands could not be clearly observed due to water molecules.

The powder X-ray diffraction pattern of the cobalt(II)-A complex is similar to zinc(II)-A in crystal structure.

B Type Complex ZnClL(HL): The infrared absorption spectra of zinc(II)-B complex is different from that of zinc(II)-A complex. In zinc(II)-B complex, some absorption bands due to $\mathrm{NH_2^+}$ vibrations could be observed in the same region as in the free ligand.

The bands which split at about 1600 $\mathrm{cm^{-1}}$ were assigned to the $\mathrm{COO^-}$ antisymmetric stretching vibrations of (*S*)-4-thiazolidinecarboxylate anion and of (*S*)-thiazolidinium-4-carboxylate, which has a zwitter ion structure, by making a comparison with the spectra of the free ligand and of zinc(II)-A.

The results of elemental analyses suggest that zinc(II)-B complex has two types of this ligand: the first is (*S*)-4-thiazolidinecarboxylate anion and the second is (*S*)-thiazolidinium-4-carboxylate, which has a zwitter ion structure.

Structure of ZnClL(HL). Crystal data are given in Table 3. The final atomic parameters are listed in Table 4.[23)] The bond lengths and bond angles are shown in Tables 5 and 6, 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 c-axis is shown in Fig. 2.

As expected from the infrared absorption spectra and the elemental analysis, the complex has two types of ligands: one is (*S*)-thiazolidinium-4-carboxylate, which assumes a zwitter ion structure, and the other is (*S*)-4-thiazolidinecarboxylate anion.

The structure of the complex consists of a one-dimensional polymer chain bridged by the carboxylate group of the anionic ligand. One carboxylate

Table 3. Crystal Data

$ZnCl(C_4H_6NO_2S)(C_4H_7NO_2S)$	
F. W.	366.18
Orthorhombic	
space group	$P2_12_12_1$
a/Å	9.719(2)
b/Å	22.194(4)
c/Å	5.8537(5)
U/Å^3	1262.6(4)
Z	4
D_m/Mg m^{-3}	1.91
D_x/Mg m^{-3}	1.93
μ(Mo $K\alpha$)/cm^{-1}	25.3

Table 5. Interatomic Distances of ZnClL(HL) with the Estimated Standard Deviations in Parentheses

Interatomic distance	l/Å	Interatomic distance	l/Å
Zn-Cl	2.369(1)	S (2)-C(5)	1.821(5)
Zn-O(1)	2.017(3)	S (2)-C(7)	1.818(5)
Zn-O(3)	2.218(3)	N(1)-C(1)	1.506(6)
Zn-N(2)	2.071(4)	N(1)-C(2)	1.496(6)
Zn-O(4)$^{\mathrm{I}}$	1.968(3)	N(2)-C(5)	1.453(7)
O(1)-C(4)	1.261(5)	N(2)-C(6)	1.471(5)
O(2)-C(4)	1.225(5)	C(2)-C(3)	1.534(6)
O(3)-C(8)	1.239(5)	C(2)-C(4)	1.534(6)
O(4)-C(8)	1.259(5)	C(6)-C(7)	1.522(6)
S (1)-C(1)	1.788(6)	C(6)-C(8)	1.536(5)
S (1)-C(3)	1.800(5)	O(1)···N(1)	2.658(5)

Key to symmetry operation: I. $0.5-x$, $-y$, $-0.5+z$.

Table 4. Final Positional Parameters (×10^4 for Non-Hydrogen Atoms; ×10^3 for Hydrogen Atoms) and Equivalent Isotropic Temperature Factors (B_{eq}/Å^2)$^{a)}$ for ZnClL(HL) with the Estimated Standard Deviations

Atom	x	y	z	B_{eq}/Å^2
Zn	1205.9(5)	−849.1(2)	1551.0(8)	1.48
Cl	−475.1(11)	−1404.7(5)	−487.7(20)	2.08
S(1)	1853.5(16)	−3122.1(6)	5813.0(28)	3.22
S(2)	−1264.2(14)	289.9(6)	6391.7(24)	2.81
O(1)	1723 (3)	−1458 (1)	3960 (5)	2.00
O(2)	3405 (4)	−1897 (2)	1969 (6)	2.52
O(3)	2400 (3)	−167 (1)	3485 (6)	1.89
O(4)	2360 (3)	819 (1)	4180 (5)	1.99
N(1)	2230 (4)	−2068 (2)	7775 (6)	1.67
N(2)	−252 (4)	−232 (2)	2641 (7)	1.72
C(1)	1602 (5)	−2673 (2)	8313 (10)	2.57
C(2)	3265 (4)	−2113 (2)	5890 (7)	1.66
C(3)	3529 (5)	−2786 (2)	5495 (9)	2.54
C(4)	2749 (4)	−1799 (2)	3718 (7)	1.55
C(5)	−648 (5)	−387 (2)	4961 (9)	2.39
C(6)	332 (4)	379 (2)	2688 (7)	1.55
C(7)	−570 (5)	778 (2)	4179 (10)	2.55
C(8)	1827 (4)	332 (2)	3520 (7)	1.45
H(31)$^{b)}$	386 (6)	−285 (3)	393 (10)	
H(32)	416 (6)	−298 (2)	663 (10)	
H(11)	68 (6)	−262 (2)	864 (10)	
H(12)	199 (6)	−287 (2)	970 (10)	
H(21)	412 (6)	−189 (2)	642 (10)	
H(N11)	274 (6)	−195 (2)	908 (9)	
H(N12)	152 (6)	−182 (2)	750 (11)	
H(N21)	−97 (6)	−23 (2)	179 (11)	
H(71)	−142 (6)	93 (2)	356 (9)	
H(72)	9 (6)	115 (2)	478 (10)	
H(51)	14 (6)	−54 (2)	591 (10)	
H(52)	−148 (6)	−65 (3)	475 (10)	
H(61)	35 (6)	53 (2)	126 (10)	

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: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$. b) The numbering scheme of hydrogen atoms is based on the number of the atom attached to the hydrogen atom.

Table 6. Bond Angles of ZnClL(HL) with the Estimated Standard Deviations in Parenthese

Bond angle	ϕ/°	Bond angle	ϕ/°
Cl-Zn-O(1)	100.09(9)	C(5)-N(2)-C(6)	107.6(4)
Cl-Zn-O(3)	166.64(9)	S (1)-C(1)-N(1)	105.7(3)
Cl-Zn-N(2)	91.6(1)	N(1)-C(2)-C(3)	106.7(3)
O(1)-Zn-O(3)	88.3(1)	N(1)-C(2)-C(4)	111.2(3)
O(1)-Zn-N(2)	113.5(1)	C(3)-C(2)-C(4)	111.8(3)
O(3)-Zn-N(2)	75.5(1)	S (1)-C(3)-C(2)	103.7(3)
O(4)$^{\mathrm{I}}$-Zn-Cl	98.7(1)	O(1)-C(4)-O(2)	127.7(4)
O(4)$^{\mathrm{I}}$-Zn-N(2)	132.8(1)	O(1)-C(4)-C(2)	116.0(4)
O(4)$^{\mathrm{I}}$-Zn-O(3)	88.1(1)	O(2)-C(4)-C(2)	116.3(4)
O(4)$^{\mathrm{I}}$-Zn-O(1)	109.8(1)	S (2)-C(5)-N(2)	108.8(3)
C(1)-S(1)-C(3)	88.7(3)	N(2)-C(6)-C(7)	109.0(3)
C(5)-S(2)-C(7)	92.4(2)	N(2)-C(6)-C(8)	108.0(3)
Zn-O(1)-C(4)	121.4(3)	C(7)-C(6)-C(8)	113.8(4)
Zn-O(3)-C(8)	112.6(3)	S (2)-C(7)-C(6)	106.0(3)
C(1)-N(1)-C(2)	111.6(3)	O(3)-C(8)-O(4)	126.0(4)
Zn-N(2)-C(5)	108.3(3)	O(3)-C(8)-C(6)	118.7(3)
Zn-N(2)-C(6)	110.6(2)	O(4)-C(8)-C(6)	115.4(3)

Key to symmetry operation: I. 0.5−*x*, −*y*, −0.5+*z*.

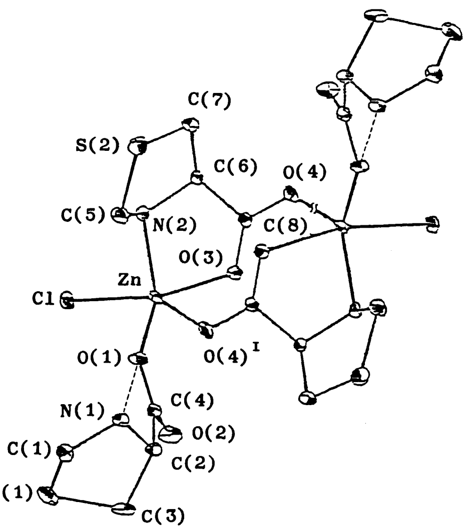

Fig. 1. The perspective drawing of ZnClL(HL) (zinc(II)-B) and the numbering scheme of non-hydrogen atoms.
-----: Hydrogen bonding.

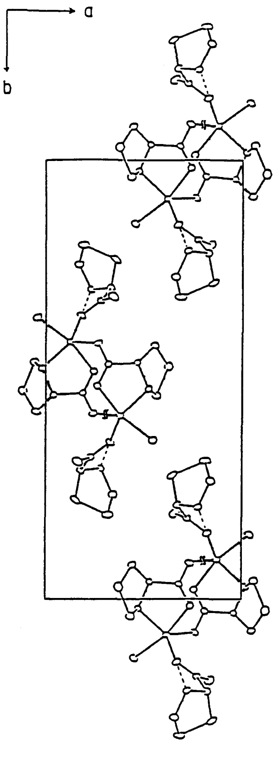

Fig. 2. The molecuar packing of ZnClL(HL) (zinc(II)-B) along the c axis. -----: Hydrogen bonding.

oxygen atom of the anionic ligand is coordinated to the zinc atom and the other is coordinated to the neighboring zinc atom to form a Zn–O–C–O–Zn bridge. This polymer chain extends in the direction of the c-axis.

The zinc atom is surrounded by five atoms: one carboxylate oxygen atom O(1) of the non-charged ligand, one carboxylate oxygen atom O(3) and one nitrogen atom N(2) of the anionic ligand, one carboxylate oxygen atom O(4)$^{\mathrm{I}}$ of the anionic ligand in the neighboring molecule, and one chlorine atom. It is novel that the same amino acid ligands have two types in one complex molecule.

This complex is in a distorted penta-coordinated trigonal bipyramidal geometry, which has a triangular plane formed by O(1), N(2), and O(4)$^{\mathrm{I}}$. The angle of Cl–Zn–O(3) is 166.64(9)°. This angle is smaller than ideal bond angle 180°.

In this geometry, the plane formed by Zn, Cl, N(2), and O(3) is a fairly flat plane, as shown in Table 7. All other least-squares planes are listed in Table 7.

The bond length of Zn–O(3), 2.218(3) Å is longest among the three Zn–O bonds; Zn–O(3), Zn–O(1) and Zn–O(4)$^{\mathrm{I}}$. The bond lengths of Zn–O(1) and Zn–O(4)$^{\mathrm{I}}$ are shorter than Tatarowski's results13) (Zn–O: 2.137(8) and 2.172(8) Å).

The bond length of Zn–N(2), 2.071(4) Å and the bond angle of O(3)–Zn–N(2) 75.5(1)° are smaller than Tatarowski's results:[13] Zn–N: 2.149(12) Å and 2.134-(12) Å, O–Zn–N: 78.1(4)°.

There are some differences in the bond lengths of the non-charged ligand and the anionic ligand, as shown in Table 5.

Let's compare the bond lengths of this complex with that of the free ligand determined by Chacko:[22] C(2)–C(4), C(6)–C(8), C(3)–S(1), and C(5)–N(2) are shorter than the corresponding bond lengths of the free ligand, while S(2)–C(5) is longer than that of the free ligand.

Table 7. Least-Squares Planes and the Deviations of Atoms (l/Å) in ZnClL(HL)

Plane(1) [$O(4)^{I}$, Zn, N(2), O(1)]
$-0.6442X-0.5692Y-0.5109Z+0.3362=0$
$O(4)^{I}$, −0.0369; Zn, 0.1896; N(2), −0.0023;
O(1), −0.0854

Plane(2) [$O(4)^{I}$, Zn, Cl, O(3)]
$-0.3915X+0.7936Y-0.4657Z+2.2329=0$
$O(4)^{I}$, 0.0095; Zn, −0.1446; Cl, 0.0721;
O(3) 0.0760

Plane(3) [O(1), Zn, Cl, O(3)]
$-0.7577X+0.2703Y+0.5940Z+0.7447=0$
O(1), −0.0227; Zn, −0.1139; Cl, 0.0816;
O(3), 0.0887

Plane(4) [N(2), Zn, Cl, O(3)]
$0.1381X+0.5548Y-0.8205Z+1.5836=0$
N(2), −0.0048; Zn, −0.0448 Cl, 0.0247;
O(3), 0.0269

Plane(5) [N(1), C(1), C(2), C(3), S(1)]
$-0.6063X+0.3747Y-0.7014Z+6.3362=0$
N(1), 0.1087; C(1), −0.2448; C(2), 0.2359;
C(3), −0.3173; S(1), 0.2595

Plane(6) [C(5), C(6), C(7), S(2)]
$-0.8269X+0.0211Y-0.5619Z+1.0038=0$
C(5), −0.1256; C(6), −0.1296; C(7), 0.1242;
S(2), −0.0689; N(2), 0.3264

Thermal Analysis and Powder X-Ray Diffraction. The reaction temperature range and the mass loss obtained from TG and DTA curves of complexes are summarized in Table 8. Nickel(II)-A and zinc(II)-A complexes give endothermic reactions below about 180 °C. In these reactions, the percentages of the mass loss for both complexes agree with the values which were calculated by assuming that two molecules of water are released in these steps. Copper(II)-A and zinc(II)-B complexes give two steps of exothermic reactions with a mass loss, as shown in Table 8.

The powder X-ray patterns of the residual materials yielded by the final exothermic reactions are very similar to those of the corresponding metal oxide, except for cadmium (II)-A complex among the A-type complexes. Cadmium(II)-A complex seems to become cadmium(II) sulfide through an exo thermic reaction.

For the zinc(II)-B complex the data suggest that in the first exothermic reaction at 206 °C this complex becomes $ZnCl_2$ and ZnO, while in the second at 465 °C only $ZnCl_2$ sublimates.

$$2\mathrm{ZnClL(HL)} \xrightarrow[\text{ca. }206\,^{\circ}\mathrm{C}]{\text{heat}} \mathrm{ZnCl_2} + \mathrm{ZnO} \xrightarrow[\text{ca. }465\,^{\circ}\mathrm{C}]{\text{heat}} \mathrm{ZnO}$$

The percentage of the mass loss calculated from this assumption is in good agreement with the experimental value, as shown in Table 8.

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Table 8. Temperature Range of Decomposition and Mass Loss

Complex	Temperature range/°C	Thermal reaction	Mass loss/%	
			Obsd	Calcd
Co(II)-A	270—297	exo		
	423—558	exo	74.3	77.0*
Ni(II)-A	116—180	endo	9.1	10.0
	246—582	exo	72.0	79.2*
Cu(II)-A	150—285	exo		
	357—459	exo	75.0	75.8*
Zn(II)-A	90—150	endo	8.8	9.8
	236—621	exo	74.1	77.5*
Cd(II)-A	200—520	exo		
	520—555	exo	57.4	61.7**
Zn(II)-B	206—228	exo		
	465—600	exo	87.8	88.9*

*as metal oxide. **as metal sulfide.

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