The Structure of Dichlorobis(L-proline)zinc(II)

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(Received July 31, 1984)

Synopsis. The title complex was prepared at pH 4.0. The crystal and molecular structures have been determined by X-ray diffraction. The crystals of $ZnCl_2(C_5H_9NO_2)_2$, F.W.=366.55, were orthorhombic: space group $P2_12_12_1$, a=13.527(3), b=16.263(3), c=6.598(1) Å, U=1451.4(5) Å^3, Z=4, D_m=1.67 g cm^{-3}, D_x=1.68 g cm^{-3}, and μ(Mo $K\alpha$)=21.2 cm^{-1}. The zinc atom is coordinated in a tetrahedral geometry to two chlorine atoms and the two carboxyl oxygen atoms of two L-proline ligands. Each L-proline is coordinated as a monodentate ligand.

The various coordination types of amino acid complexes are important for the discussion of the different metal-binding site models on proteins. Many complexes should be prepared under different conditions. However, most of the complexes with amino acids have been prepared under neutral or basic conditions. Therefore, we tried to prepare amino acid complexes at low pH, in order to study different coordination types from ones under neutral or basic conditions. In this work, as part of the program, a zinc complex of L-proline (Hpro) was prepared at low pH and the structure was determined in order to compare it with the cadmium complexes having analogous amino acid ligands.[1,2]

Experimental

Preparation of Dichlorobis(L-proline)zinc(II). To an aqueous solution of 4.61 g (0.04 mol) of Hpro, 2.73 g (0.02 mol) of $ZnCl_2$ was added. Then the solution (pH 4.0) was stirred for several hours on a water bath at 50—60 °C. Clear colorless prisms were obtained by standing at room temperature; they were air-dried. Found: C, 32.50; H, 4.90; N, 7.50; Zn, 17.7%. Calcd for $ZnCl_2(C_5H_9NO_2)_2$: C, 32.76; H, 4.96; N, 7.74; Zn, 17.84%. An almost quantitative yield of the complex was obtained.

X-Ray Measurements. The reflection intensities were collected by the θ—2θ scan technique ($2\theta \leqq 60°$) on a Philips PW1100 automated four-circle diffractometer. The intensities ($|F_o| \geqq 3\sigma(|F_o|)$) were corrected for Lorentz and polarization factors, but not for absorption, because of the low magnitude of μr (=0.25). All calculations were carried out on a HITAC M-280H computer at the Computer Center of The University of Tokyo, using the local version of UNICS.[3] The scattering factors were taken from tables.[4]

Structure Determination. The structure was solved by a heavy-atom method and refined by a block-diagonal least-squares method. The weighting scheme was $W=1/[\{\sigma(|F_o|)\}^2+(0.045\times|F_o|)^2)$. The final R value[5] was 0.035, with anisotropic temperature factors for all the non-hydrogen atoms.

Results and Discussion

The final atomic coordinates and the equivalent isotropic temperature factors, except for those of calculated hydrogen atoms, are shown in Table 1. The bond lengths and bond angles are in Table 2.[6]

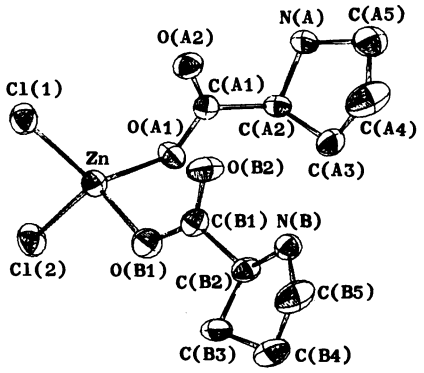

Fig. 1. The perspective drawing of the complex and the numbering scheme.

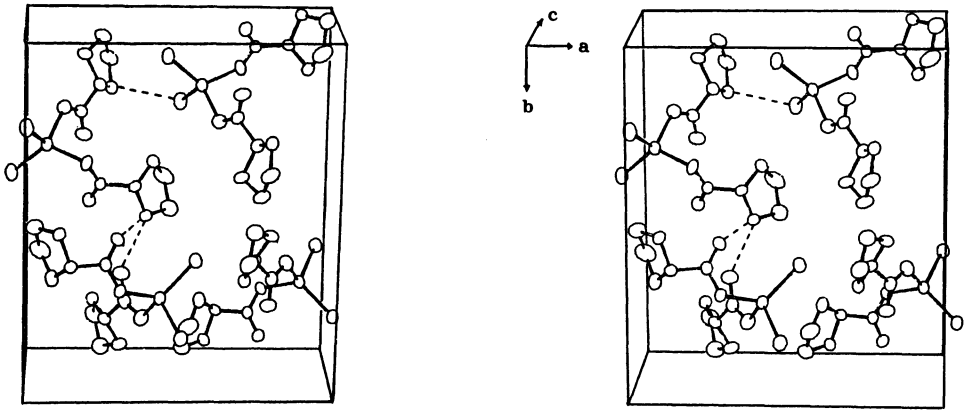

Fig. 2. The crystal packing diagram of $ZnCl_2(Hpro)_2$. (----: Hydrogen bonding)

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors, with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2 a)
Zn	690.4(3)	1822.9(3)	1475.5(7)	2.46
Cl(1)	−450.1(7)	920.1(7)	444(2)	3.55
Cl(2)	56.3(8)	2569.5(8)	4087(2)	3.72
O(A1)	1965(2)	1460(2)	2664(5)	2.84
O(A2)	2049(2)	236(2)	1148(5)	3.13
N(A)	3888(3)	−58(2)	2296(7)	2.84
C(A1)	2411(3)	806(2)	2075(6)	2.15
C(A2)	3516(3)	806(2)	2600(7)	2.37
C(A3)	4112(3)	1322(3)	1112(9)	3.76
C(A4)	4489(5)	740(4)	−438(8)	4.97
C(A5)	4664(4)	−49(3)	664(8)	4.19
O(B1)	1230(2)	2646(2)	−405(5)	3.47
O(B2)	1879(3)	1661(2)	−2338(6)	3.75
N(B)	2788(2)	2733(2)	−4826(6)	2.78
C(B1)	1772(3)	2377(3)	−4826(6)	2.69
C(B2)	2396(3)	3034(2)	−2825(7)	2.58
C(B3)	1895(4)	3842(2)	−3334(9)	3.75
C(B4)	2496(4)	4165(3)	−5103(11)	4.93
C(B5)	2703(4)	3415(3)	−6360(8)	4.40

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

A perspective drawing of the complex, with the numbering scheme, is shown in Fig. 1 and the crystal packing diagram in Fig. 2.

As shown in Fig. 1, the zinc atom is coordinated in a tetrahedral geometry to two chlorine atoms and two carboxyl oxygen atoms of two L-proline ligands: each of them is a zwitter ion. The angles around the zinc atom are not exactly tetrahedral angles, as shown in Table 2.

The nitrogen atom, N(A), is associated with two intermolecular hydrogen bonds, N(A)···O(A2)^{I} (2.856(6) Å) and N(A)···O(B2)^{I} (2.815(5) Å), as shown in Fig. 2. On the other hand, N(B) seems to connect only with Cl(2)^{II} *via* a hydrogen bond (N(B)···Cl(2)^{II}; 3.145(5) Å).[7] The difference of the intermolecular hydrogen bonds reflects the difference of the shapes of the two pyrrolidine rings. By these intermolecular hydrogen bonds, the complex molecules are connected to each other in three dimensions.

The system is different from those of $CdCl_2$(Hhpro) and $CdCl_2$(Hpro)·H_2O.[1,2] Both consist of one-dimensional polymers bridged by chlorine atoms and a carboxyl group, and the ligand 4-hydroxy-L-proline (Hhpro) or Hpro is coordinated to the metal with only carboxyl oxygen atoms as a zwitter ion. The polymers are aligned in parallel by hydrogen bonds or van der Waals' contacts in the crystals.

Table 2. Bond lengths and bond angles, with estimated standard deviations in parentheses

Bond length	l/Å	Bond length	l/Å
Zn-Cl(1)	2.234(2)	Zn-Cl(2)	2.275(1)
Zn-O(A1)	1.984(3)	Zn-O(B1)	1.967(3)
O(A1)-C(A1)	1.282(5)	O(B1)-C(B1)	1.265(5)
O(A2)-C(A1)	1.213(5)	O(B2)-C(B1)	1.223(5)
C(A1)-C(A2)	1.535(5)	C(B1)-C(B2)	1.515(6)
C(A2)-C(A3)	1.523(7)	C(B2)-C(B3)	1.516(6)
C(A3)-C(A4)	1.484(8)	C(B3)-C(B4)	1.518(9)
C(A4)-C(A5)	1.494(8)	C(B4)-C(B5)	1.501(8)
C(A5)-N(A)	1.505(7)	C(B5)-N(B)	1.507(6)
N(A)-C(A2)	1.505(5)	N(B)-C(B2)	1.505(6)
Bond angle	ϕ/°	**Bond angle**	ϕ/°
Cl(1)-Zn-Cl(2)	108.65(5)	O(A1)-Zn-O(B1)	97.47(13)
Cl(1)-Zn-O(A1)	121.61(9)	Cl(1)-Zn-O(B1)	120.76(11)
Cl(2)-Zn-O(A1)	100.81(9)	Cl(2)-Zn-O(B1)	104.76(11)
O(A1)-C(A1)-O(A2)	126.6(4)	O(B1)-C(B1)-O(B2)	127.1(4)
O(A1)-C(A1)-C(A2)	113.0(3)	O(B1)-C(B1)-C(B2)	113.8(4)
O(A2)-C(A1)-C(A2)	120.3(3)	O(B2)-C(B1)-C(B2)	119.0(4)
C(A1)-C(A2)-C(A3)	111.7(4)	C(B1)-C(B2)-C(B3)	117.4(3)
C(A1)-C(A2)-N(A)	107.2(3)	C(B1)-C(B2)-N(B)	110.6(3)
C(A3)-C(A2)-N(A)	104.6(3)	C(B3)-C(B2)-N(B)	104.2(3)
C(A2)-C(A3)-C(A4)	106.0(4)	C(B2)-C(B3)-C(B4)	103.4(4)
C(A3)-C(A4)-C(A5)	105.5(5)	C(B3)-C(B4)-C(B5)	104.1(4)
C(A4)-C(A5)-N(A)	104.3(4)	C(B4)-C(B5)-N(B)	104.0(4)

The difference of the crystal structures results from the halogeno zinc or cadmium complexes retaining the traces of the zinc or cadmium halide: zinc and cadmium chlorides consist of $ZnCl_4$ tetrahedra and $CdCl_6$ octahedra, respectively. In aqueous solutions of cadmium halides, there are significant amounts of the undissociated halides and polymeric species, as is well known.

The authors wish to express their thanks to Professor Yoichi Iitaka of The University of Tokyo for the collection of the intensity data. They would also like to thank Dr. F. S. Howell of Sophia University for correcting this manuscript.

References

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

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

5) $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$

6) The final atomic parameters containing calculated hydrogen atoms, the final F_o—F_c values, and some additional data are deposited as Document No. 8522 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

7) Key to symmetry operations: I. 0.5−x, −y, 0.5+z; II. 0.5+x, 0.5−y, −z.