Crystal Structure of [μ-*N*,*N*′-Bis(salicylidene)-1,3-propanediaminato-methanolatozinc(II)]dichlorozinc(II) Homodinuclear Complex Methanol Solvate

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Zinc has been known for long time to be an essential element in living organisms and to activate more than 60 enzymes.[1] Although there is strong evidence indicating an active involvement of zinc in child-growth[1–3], to the best of our knowledge, little, if any, is known concerning the storage mechanism of this element.

In this work, a zinc-Schiff base complex having a dinuclear structure was prepared and characterized by X-ray crystallography. The ligand, bis-*N*,*N*′-salicylidene-1,3-diaminopropane was previously shown to give a complex of similar structure with Cu(II) ion, namely, a compoud with the composition CuL·$CuCl_2$, L being the aforementioned ligand.[4] An equimolar mixture of $ZnCl_2$ and the ligand in methanol resulted in crystals of the composition ZnL·$ZnCl_2$·2MeOH, instead of a simple one-to-one complex, ZnL, expected at first sight.

Preparation: *N*,*N*′-bis-salicylidene-1,3-diaminopropane (0.282 g, 1 mmol) was dissolved in 50 ml MeOH by heating. Into this solution was added a solution of $ZnCl_2$ (0.272 g, 2 mmol) in 30 ml hot MeOH. The mixture was set aside for 3 – 4 d. The precipitated crystals were filtered and used for X-ray data collection.

Crystal and experimental data are given in Table 1, while the final atomic parameters are given in Table 2. Some of the important coordinative bonds are given in Table 3. As shown in Fig. 2, one of the two zinc atoms has five coordination, while the other has four coordination. The bond lengths and angles show that both coordinations are not ideal. The question arises as to whether the five coordination around Zn2 can be described as a distorted square pyramid or a distorted trigonal bipyramid. For this purpose, an index (τ) is defined in terms of the two largest angles (α and β), between the bonds around the central atoms as

$$\tau=(\beta-\alpha)/60$$

If τ is equal to 0, the coordination is ideal square pyra-

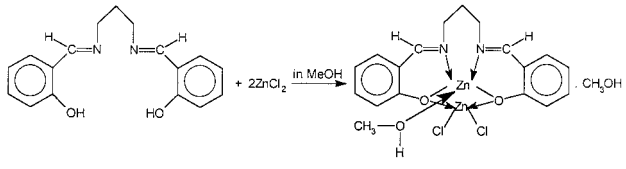

Fig. 1 Scheme of reaction.

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Table 1 Crystal and experimental data

Formula: $C_{19}H_{23}Cl_2Zn_2N_2O_4$	
Formula waight=541.02	
Crystal system: monoclinic	
Space group: $P2_1$	Z=2
a=9.9247(8)Å	
b=8.9188(12)Å	
c=13.8143(18)Å	
β=109.07(1)°	
V=1155.8(3)Å^3	
D_x=1.5552 g/cm^3	
μ(Mo K$_\alpha$)=2.3815 mm^{-1}	
T=295 K	
Colorless	
F(0 0 0)=546	
Crystal size: 0.300×0.125×0.050 mm	
Radiation=Mo K$_\alpha$	
$2\theta_{max}$=53.4°	
No. of reflection used=2266	
No. of parameters=285	
R=0.0617	
R_w=0.0701	
Goodness-of-fit=1.03	
$(\Delta/\sigma)_{max}$=0.0010	
$(\Delta\rho)_{max}$=1.311 eÅ^{-3}	
$(\Delta\rho)_{min}$=–0.217 eÅ^{-3}	
Measurements: Enraf Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: MolEN	
Treatment of hydrogen atoms: H atoms of the phenyl rings were placed geometrically 0.95 Å from their corresponding C atoms, while the H atoms of C8, C10 and methyl groups were located in a difference map and refined for a few cycles. For all H atoms a riding model was used. Due to the disordering on C9 atom we could not coordinate any hydrogen to it.	
Refinement: full matrix least-squares (MolEN)	

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Zn1	1.1036(1)	0.0433(2)	0.7787(1)	3.67(2)
Zn2	0.8870(1)	0.29930(9)	0.76682(9)	3.42(2)
*Cl*1	1.1389(4)	-0.1578(4)	0.8783(3)	6.3(1)
*Cl*2	1.2355(3)	0.0689(6)	0.6792(3)	6.7(1)
O1	1.0875(7)	0.235(1)	0.8480(6)	4.1(2)
O2	0.8989(7)	0.0838(9)	0.7135(6)	3.9(2)
O3	0.9094(9)	0.410(1)	0.6459(6)	4.8(2)
O4	0.888(1)	0.116(1)	0.303(1)	8.3(3)
N1	0.909(1)	0.472(1)	0.8663(7)	3.8(2)
N2	0.6730(9)	0.267(1)	0.7325(8)	4.5(2)
C1	1.188(1)	0.305(2)	0.9172(7)	3.6(2)
C2	1.331(1)	0.255(2)	0.951(1)	4.6(3)
C3	1.437(1)	0.320(2)	1.0285(9)	5.3(3)
C4	1.406(1)	0.443(2)	1.081(1)	6.7(4)
C5	1.269(1)	0.495(2)	1.048(1)	5.7(4)
C6	1.160(1)	0.433(1)	0.9690(8)	3.9(2)
C7	1.021(1)	0.502(1)	0.9398(9)	4.4(3)
C8	0.784(1)	0.570(2)	0.852(1)	6.4(4)
C9	0.655(4)	0.530(6)	0.783(3)	4.5(8)
C9'	0.645(2)	0.472(2)	0.844(1)	4.9(4)
C10	0.591(2)	0.400(2)	0.752(1)	7.2(4)
C11	0.602(1)	0.154(2)	0.692(1)	4.5(3)
C12	0.651(1)	0.019(1)	0.6549(9)	3.9(2)
C13	0.548(1)	-0.087(2)	0.604(1)	4.8(3)
C14	0.579(1)	-0.211(2)	0.560(1)	6.3(4)
C15	0.719(1)	-0.239(2)	0.568(1)	5.7(3)
C16	0.825(1)	-0.139(2)	0.618(1)	4.9(3)
C17	0.796(1)	-0.005(1)	0.6635(8)	3.4(2)
C18	0.899(2)	0.338(2)	0.552(1)	7.8(5)
C19	0.752(2)	0.075(3)	0.299(2)	12.5(8)

$B_{eq}=(8\pi^2/3)\ \Sigma_i\Sigma_j U_{ij}\ a_i^*a_j^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

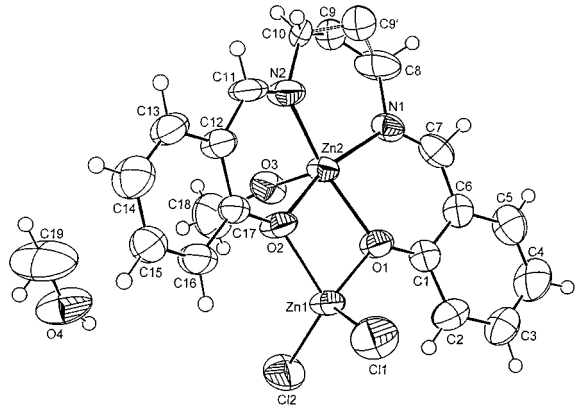

Fig. 2 ORTEP drawing of the title compound with atom labeling.

mid, and if τ is equal to 1, the coordination is ideal trigonal bipyramid.[5] As can be seen from Table 3, the two largest angles around the Zn2 atom are O1–Zn2–N2 159.6° and O2–Zn2–N1 148.4°. Thus, τ can be calculated as 0.1866. This result shows that five coordination is a distorted square pyramid. As can be easily seen from Fig. 2, the coordination of the Zn(II) atom is distorted tetrahedral. Both coordinations for zinc are common coordination.[3,6] In the complex, the bond lengths exhibit values of 2.216(4), 2.200(4)Å for Zn–Cl, 1.993(9), 1.968(6), 2.021(7) and 2.073(8)Å for Zn–O and 2.02(1), 2.039(9)Å for Zn–N and all values are in agreement with those cited in the literature.[3,6]

Table 3 Selected bond distances (Å) and angles (°)

Zn1	*Cl*1	2.216(4)		O4	C19	1.38(2)	
Zn1	*Cl*2	2.200(4)		N1	C7	1.27(1)	
Zn1	O1	1.993(9)		N1	C8	1.48(2)	
Zn1	O2	1.968(6)		N2	C10	1.51(2)	
Zn2	O1	2.021(7)		N2	C11	1.25(2)	
Zn2	O2	2.073(8)		C6	C7	1.44(2)	
Zn2	O3	2.014(9)		C8	C9	1.37(4)	
Zn2	N1	2.02(1)		C8	C9'	1.60(2)	
Zn2	N2	2.039(9)		C9	C10	1.32(5)	
O1	C1	1.29(1)		C9'	C10	1.37(3)	
O2	C17	1.30(1)		C11	C12	1.46(2)	
O3	C18	1.42(2)					

Cl1	Zn1	*Cl2*	117.8(2)	Zn2	N2	C10	115.8(8)		
Cl1	Zn1	O1	114.6(3)	Zn2	N2	C11	127.3(9)		
Cl1	Zn1	O2	111.2(3)	C10	N2	C11	117.(1)		
Cl2	Zn1	O1	111.7(3)	O1	C1	C2	123.(1)		
Cl2	Zn1	O2	115.6(3)	O1	C1	C6	121.3(9)		
O1	Zn1	O2	80.2(3)	C1	C6	C7	122.0(9)		
O1	Zn2	O2	77.1(3)	C5	C6	C7	119.(1)		
O1	Zn2	O3	104.0(4)	N1	C7	C6	130.(1)		
O1	Zn2	N1	88.3(3)	N1	C8	C9	119.(2)		
O1	Zn2	N2	148.4(4)	N1	C8	C9'	110.(1)		
O2	Zn2	O3	97.0(4)	C9	C8	C9'	39.(2)		
O2	Zn2	N1	159.6(3)	C8	C9	C9'	83.(3)		
O2	Zn2	N2	88.0(4)	C8	C9	C10	135.(4)		
O3	Zn2	N1	100.3(4)	C9'	C9	C10	71.(3)		
O3	Zn2	N2	105.4(4)	C8	C9'	C9	58.(2)		
N1	Zn2	N2	97.7(4)	C8	C9'	C10	113.(2)		
Zn1	O1	Zn2	101.2(3)	C9	C9'	C10	65.(3)		
Zn1	O1	C1	126.9(7)	N2	C10	C9	121.(2)		
Zn2	O1	C1	131.4(8)	N2	C10	C9'	117.(1)		
Zn1	O2	Zn2	100.2(3)	C9	C10	C9'	44.(2)		
Zn1	O2	C17	130.1(7)	N2	C11	C12	129.(1)		
Zn2	O2	C17	129.0(7)	C11	C12	C17	123(1)		
Zn2	O3	C18	123(1)	O2	C17	C12	123.(1)		
Zn2	N1	C7	125.2(9)	O2	C17	C16	121(1)		
Zn2	N1	C8	117.6(7)	C7	N1	C8	117.(1)		

As shown from Fig. 2, the hydrogen atoms of the C9 atom were not included in the calculations. During the early stage of refinement, disorder was evident for C9. There observed two peaks for C9 (total multiplicity 1.000). A resolution of the disorder was possible by keeping the free thermal parameters and bond lengths, and was made by restraining the multiplicity of the C9 and C9′ atoms (0.300 and 0.700). The displacement ellipsoids are drawn at the 25% probability level.

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