



Synthesis and Supramolecular Structure of *Bis*-zinc(II) Tetraformate Tetrahydrate Polymer $[Zn_2(HCOO^-)_4(H_2O)_4]_n$

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The polymeric compound *bis*-zinc(II) tetraformate tetrahydrate with the m.f. $[Zn_2(HCOO^-)_4(H_2O)_4]_n$, was synthesized unexpectedly by the reaction of zinc(II) acetate dihydrate with 2,2'-[1,1'-(propane-1,3-diylldioxy)*bis*(nitrilomethylidyne)]di-1-naphthol (H_2L) in ethanol. The molecule crystallizes in the monoclinic system, adopts a polymer conformation. The crystal structure indicates that it is an infinite three-dimension supramolecular network complex.

Key Words: Monooxime compound, Synthesis, Crystal structure, Supramolecular interaction.

INTRODUCTION

Salen-type compound is a chelate ligand consisting of two nitrogen and two oxygen donors, capable of forming stable metal complexes¹⁻³. Various functional Salen-metal complexes have been synthesized by complexation with the appropriate metal sources⁴⁻⁷. And salen-metal complexes can be used to obtain non-linear optical materials⁸, biological systems⁹, interesting magnetic properties¹⁰ and building blocks for cyclic supramolecular structures¹¹. In this paper, complexation between a Salen-type bisoxime ligand H_2L (2,2'-[1,1'-(propane-1,3-diylldioxy)*bis*(nitrilomethylidyne)]di-1-naphthol) and zinc(II) acetate dihydrate has been studied. However, it is remarkable that the desired complex $[Zn(L)]$ was not gained, but an unexpected *bis*-zinc(II) tetraformate tetrahydrate polymer $[Zn_2(HCOO^-)_4(H_2O)_4]_n$, was obtained.

EXPERIMENTAL

2-Hydroxybenzaldehyde was purchased from Alfa Aesar and used without further purification. 1,3-*Bis*(aminoxy)propane was synthesized according to an analogous method reported earlier³. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra in the range 4000-400 cm^{-1} were recorded on a VERTEX70 FT-IR spectrophotometer using KBr pellets. The ¹H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. X-Ray single crystal structure was determined

on a Bruker Smart 1000 CCD area detector. Melting points were measured by the use of a microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and the thermometer was uncorrected.

General procedure: 2,2'-[1,1'-(Propane-1,3-diylldioxy)*bis*(nitrilomethylidyne)]di-1-naphthol (H_2L): A solution of 1,3-*bis*(aminoxy)propane (106.2 mg, 1 mmol) in ethanol (5 mL) was added to a solution of 1-hydroxy-2-naphthaldehyde (344.8 mg, 2 mmol) in hot ethanol (5 mL) and the mixture was stirred at 328 K for 5 h. After cooling to room temperature, colourless precipitates were collected on a suction filter, washed with ethanol and ethanol/hexane (1:4), respectively. The isolated compound was dried under reduced pressure and purified with recrystallization from ethanol to yield 259.4 mg of crystalline solid. Yield 62.6 %. m.p. 393-395 K. Anal. calcd. (%) for: $C_{25}H_{22}N_2O_4$: C, 72.45; H, 5.35; N, 6.76. Found (%): C, 72.23; H, 5.42; N, 6.87.

The unexpected present polymeric complex, biszinc(II) tetraformate tetrahydrate polymer, $[Zn_2(HCOO^-)_4(H_2O)_4]_n$ was prepared from 2,2'-[1,1'-(propane-1,3-diylldioxy)*bis*(nitrilomethylidyne)]di-1-naphthol (H_2L) and zinc(II) acetate dihydrate. A solution of Zn(II) acetate dihydrate (5.2 mg, 0.024 mmol) in ethanol (6 mL) was added dropwise to a solution of H_2L (9.9 mg, 0.023 mmol) in THF (5 mL) at room temperature. The colour of the mixing solution turned to yellow immediately, the mixture was filtered and the filtrate was allowed to stand at room temperature for three weeks. Then the solvent partially evaporated and white prismatic single crystals suitable for X-ray analysis were obtained. Yield 35.7 %. Anal. calcd. (%)

for $C_4H_{12}O_{12}Zn_2$ ($[Zn_2(HCOO)_4(H_2O)_4]_n$): C, 12.55; H, 3.16; Zn, 34.15. Found (%): C, 12.42; H, 3.07; Zn, 34.32.

X-Ray structure determination: The single crystal of the title polymeric complex, with approximate dimensions of 0.33 mm × 0.30 mm × 0.25 mm was placed on a Bruker Smart 1000 diffractometer equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 298(2) K. The structure was solved by using the program SHELXS-97¹² and Fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97¹³. Details of the data collection and refinements of title compound are given in Table-1. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. CCDC: 684099.

TABLE-1
CRYSTAL DATA AND REFINEMENT
PARAMETERS FOR THE TITLE COMPLEX

Empirical formula	$C_4H_{12}O_{12}Zn_2$
Formula weight	382.88
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Cell dimensions	$a = 8.6501(10)$ Å, $b = 7.1269(8)$ Å, $c = 9.2852(13)$ Å, $\beta = 97.5800(10)$
Volume	$567.42(12)$ Å ³
Z	2
Density (calculated)	2.241 mg/m ³
Absorption coefficient	4.287 mm ⁻¹
$F_{(000)}$	384
Index ranges	$-7 \leq h \leq 10$, $-8 \leq k \leq 8$, $-11 \leq l \leq 10$
Reflections collected	2577
Independent reflections	983 [$R_{int} = 0.0935$]
Data/restraints/parameters	983/0/85
Goodness of fit indicator	0.981
R [$I > 2\sigma(I)$]	$R_1 = 0.0444$, $wR_2 = 0.1110$
Largest diff. peak and hole	0.728 and -0.724 e. Å

RESULTS AND DISCUSSION

X-Ray crystallographic analysis revealed the crystal structure of title complex. And the structure is shown in Fig. 1. Selected bond distances and angles are listed in Table-2. The crystal structure of the title complex is built up by $Zn_2(HCOO)_4(H_2O)_4(C_4H_{12}O_{12}Zn_2)$ structural units, in which all bond lengths are in normal ranges. The molecule crystallizes in the monoclinic system, adopts a polymer conformation. The zinc(II) (Zn1 and Zn2) ions linked by formate anions which coordinate to the two zinc(II) ions *via* a familiar Zn1-O-C-O-Zn2 coordinated mode. In the title complex, all the zinc(II) ions are six-coordinated forming a slightly distorted octahedral environment. The zinc(II) (Zn1) ion is six-coordinated by oxygen (O1, O3, O4, O1A, O3A and O4A) atoms from six formate anion groups. The O3, O3A, O4 and O4A atoms could be located in the equatorial plane and the two axial bonds form a straight line through the metal center ($\angle O1-Zn1-O1A$, 180°). The axial Zn1-O1 bond length ($2.134(3)$ Å) is longer by 0.076 Å than the Zn1-O3 bond length ($2.058(4)$ Å) and by 0.042 Å than the Zn1-O4 bond length ($2.092(3)$ Å). All the bond angles in the equatorial plane are very close to right angles ($\angle O1-Zn1-O3$, 87.33° ; $\angle O1-Zn1-O4$, 87.23°). Another zinc(II) (Zn2) ion also coordinates to six oxygen (O5, O6, O2, O5A, O6A and O2A) atoms to form a slightly distorted octahedron, four oxygen (O5, O6, O5A and O6A) atoms coming from four coordinated water molecules and two oxygen (O2 and O2A) atoms belonging to two coordinated formates. The O5, O5A, O6 and O6A atoms could be located in the equatorial plane and the two axial bonds also form a straight line through the zinc(II) center ($\angle O2-Zn2-O2A$, 180°). The axial Zn2-O2 bond length ($2.153(4)$ Å) is longer by 0.104 Å than the Zn2-O5 bond length ($2.049(4)$ Å) and by 0.061 Å than the Zn2-O6 bond length ($2.092(4)$ Å). The bond angles in the equatorial plane also approximate to right angles ($\angle O2-Zn2-O6$, 91.44° ; $\angle O2-Zn2-O5$, 89.84°). The crystal structure indicates that it is an infinite three-dimension network complex.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES ($^\circ$) FOR THE TITLE COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Zn(1)-O(3)	2.058(4)	Zn(1)-O(1)	2.134(3)	Zn(2)-O(2)	2.153(4)
Zn(1)-O(3) ^{#1}	2.058(4)	Zn(2)-O(5) ^{#4}	2.049(3)	Zn(2)-O(2) ^{#4}	2.153(4)
Zn(1)-O(4) ^{#2}	2.091(3)	Zn(2)-O(5)	2.049(3)	O(4)-Zn(1) ^{#5}	2.091(3)
Zn(1)-O(4) ^{#3}	2.091(3)	Zn(2)-O(6)	2.092(4)	—	—
Zn(1)-O(1) ^{#1}	2.134(3)	Zn(2)-O(6) ^{#4}	2.092(4)	—	—
Bond	Angles	Bond	Angles	Bond	Angles
O(3)-Zn(1)-O(3) ^{#1}	180.00	O(4) ^{#2} -Zn(1)-O(1)	92.77(13)	O(6) ^{#4} -Zn(2)-O(2)	91.43(13)
O(3)-Zn(1)-O(4) ^{#2}	90.48(13)	O(4) ^{#3} -Zn(1)-O(1)	87.23(13)	O(5) ^{#4} -Zn(2)-O(2) ^{#4}	89.84(17)
O(3) ^{#1} -Zn(1)-O(4) ^{#2}	89.52(13)	O(1) ^{#1} -Zn(1)-O(1)	180.000	O(5)-Zn(2)-O(2) ^{#4}	90.16(17)
O(3)-Zn(1)-O(4) ^{#3}	89.52(13)	O(5) ^{#4} -Zn(2)-O(5)	180.000	O(6)-Zn(2)-O(2) ^{#4}	91.43(13)
O(3) ^{#1} -Zn(1)-O(4) ^{#3}	90.48(13)	O(5) ^{#4} -Zn(2)-O(6)	90.76(14)	O(6) ^{#4} -Zn(2)-O(2) ^{#4}	88.57(13)
O(4) ^{#2} -Zn(1)-O(4) ^{#3}	180.0	O(5)-Zn(2)-O(6)	89.24(14)	O(2)-Zn(2)-O(2) ^{#4}	180.000
O(3)-Zn(1)-O(1) ^{#1}	87.32(14)	O(5) ^{#4} -Zn(2)-O(6) ^{#4}	89.24(14)	C(1)-O(1)-Zn(1)	127.4(4)
O(3) ^{#1} -Zn(1)-O(1) ^{#1}	92.68(14)	O(5)-Zn(2)-O(6) ^{#4}	90.76(14)	C(1)-O(2)-Zn(2)	133.0(4)
O(4) ^{#2} -Zn(1)-O(1) ^{#1}	87.23(13)	O(6)-Zn(2)-O(6) ^{#4}	180.0	C(2)-O(3)-Zn(1)	122.1(3)
O(4) ^{#3} -Zn(1)-O(1) ^{#1}	92.77(13)	O(5) ^{#4} -Zn(2)-O(2)	90.16(17)	C(2)-O(4)-Zn(1) ^{#5}	125.8(3)
O(3)-Zn(1)-O(1)	92.68(14)	O(5)-Zn(2)-O(2)	89.84(17)	—	—
O(3) ^{#1} -Zn(1)-O(1)	87.32(14)	O(6)-Zn(2)-O(2)	88.57(13)	—	—

Symmetry transformations used to generate equivalent atoms: ^{#1}-x+2, -y+1, -z+1; ^{#2}-x+2, y+1/2, -z+3/2; ^{#3}x, -y+1/2, z-1/2; ^{#4}-x+1, -y+2, -z+1; ^{#5}-x+2, y-1/2, -z+3/2.

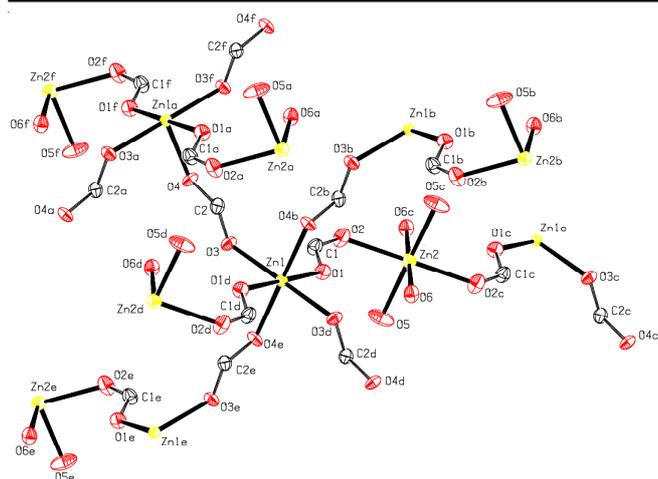


Fig. 1. Molecular structure of the title complex with atom numbering scheme. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30% probability level

The introduction of coordinated water molecules successfully leads to the assembly of the complex by intermolecular hydrogen bonds. As illustrated in Fig. 2, the intramolecular O6-H6A...O1 hydrogen bonds involving the hydroxyl groups and formic acid oxygen atoms generate S(6) ring motifs. Moreover, the intermolecular O6-H6B...O3 and O5-H5B...O4 hydrogen bonds link neighbouring molecules into $R_2^2(8)$ ring graph-motifs and form an infinite 2D-layer supramolecular structure on the *ab* crystallographic plane (Fig. 3). Simultaneously, this linkage is further stabilized by the intermolecular O5-H5A...O2 hydrogen bonds to form an infinite three-dimensional supramolecular network structure (Table-3, Fig. 4).

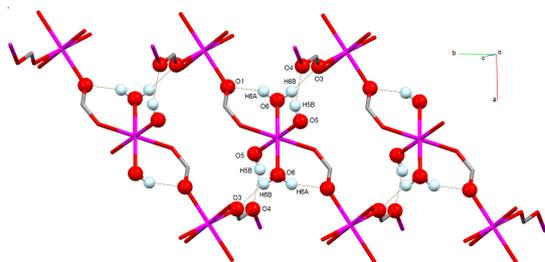


Fig. 2. View of S(6) and $R_2^2(8)$ ring motifs generated by intramolecular and intermolecular hydrogen bonds of the title complex

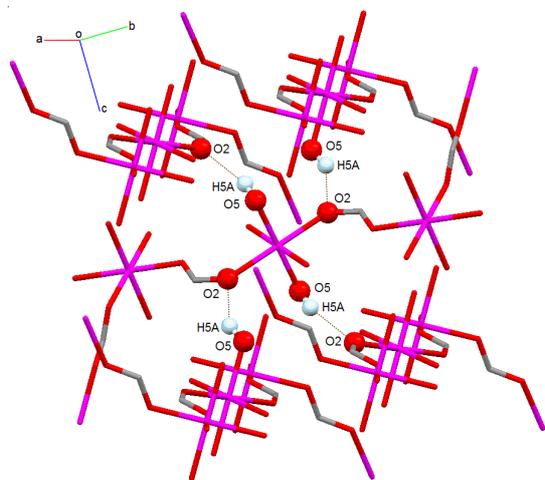


Fig. 3. View of an infinite 2D-layer supramolecular structure of the title complex on the *ab* crystallographic plane

TABLE-3
HYDROGEN-BONDING DATA [Å, °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠D-H...A
O5-H5A...O2	0.85	1.98	2.725 (5)	145
O5-H5B...O4	0.85	2.00	2.773(5)	150
O6-H6A...O1	0.85	1.95	2.739(5)	155
O6-H6B...O3	0.85	1.94	2.774(5)	168

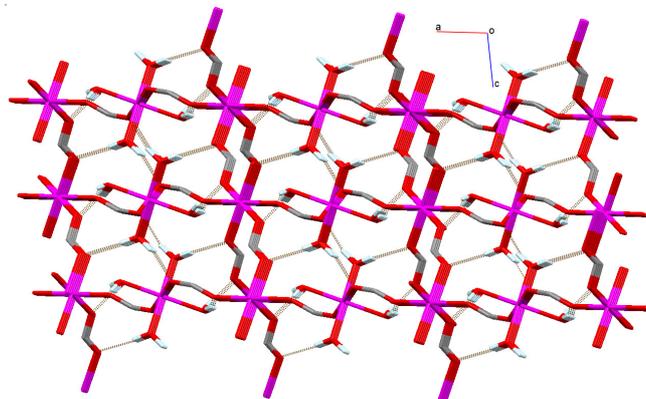


Fig. 4. View of an infinite 3D supramolecular network of the title complex

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