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Synthesis, Structure and Spectral Properties of Tetranuclear Zn(II) Complex Based on 2-Hydroxy-3-methoxybenzaldehyde

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A supramolecular tetranuclear Zn(II) complex, $[(ZnL)_2(AcO)_2\{Zn(EtOH)\}_2]$ (H_3L = 6-methoxy-6'-hydroxy-2,2'-[ethylenediyldioxy*bis*-(nitrilomethylidyne)]diphenol), has been synthesized and characterized structurally. The structure of the Zn(II) complex consists of four Zn(II) atoms, two tridentate L^{3-} units, two acetate ions and two coordinated ethanol molecules. All of the Zn(II) ions in the Zn(II) complex are five-coordinated and have slightly distorted tetragonal pyramidal geometry and pentahedral geometry, respectively. Moreover, every Zn(II) complex molecule links other molecules into an infinite 3D supramolecular structure *via* intermolecular C-H···O interactions and C-H···π interactions.

Keywords: Asymmetric Salamo-type ligand, Zn(II) complex, Crystal structure.

INTRODUCTION

Oxime-type ligands and their complexes have been playing an important part in the development of modern coordination chemistry[1]. 6-Methoxy-6'-hydroxy-2,2'-[ethylenediyldioxy-*bis*(nitrilomethylidyne)]diphenol is a N_2O_2-type bisoxime compound, which has potential to form different types of complexes due to tautomeric effect of enolic form and ketonic form[2]. Oxime-type compounds have recently attracted much attention because they are used extensively in the sterilization, mimic enzyme catalysis activity and antivirus[3-7]. At present, a significant increase in the research of the transition metal complexes with these series of oxime-type ligands has been observed and these complexes have been widely used in many areas, such as chelators[8], luminescent materials[9-11], metallurgy, dyes, dioxygen carriers, oxygen transport[12] and catalysts for the oxygenation reactions of organic molecules[13], also widely applied to mimic cobalamin (B_{12}) coenzymes[14], herein, a new asymmetric salamo-type bisoxime ligand (H_3L) and its Zn(II) complex have been synthesized and structurally characterized.

EXPERIMENTAL

2-Hydroxy-3-methoxybenzaldehyde (≥ 98 %) and 2,3-dihydroxybenzaldehyde were purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analysis for Zn(II) was detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FT-IR spectra were recorded on a VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-400 cm^{-1}). UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer in 1×10^{-5} mol/L CH_2Cl_2 solution. ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature. Melting points were obtained by use of an X_4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

Synthesis of H_3L: 1,2-*bis*(Aminooxy)ethane was synthesized by reported method[15]. Yield, 52.7 %. Anal. Calcd for $C_2H_8N_2O_2$ (%): C, 26.08; H, 8.76; N, 30.42; found (%): C, 25.92; H, 8.87; N, 30.39. ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.79 (s, 4H), 5.52 (s, 4H). 2-[*O*-(1-ethyloxyamide)]oxime-6-methoxyphenol was synthesized according to an analogous method reported previously in the literature[16]. The ligand 6-methoxy-6'-hydroxy-2,2'-[ethylenediyldioxy*bis*(nitrilo-methylidyne)]diphenol (H_3L) was synthesized with a slightly modified method reported literature[16].

Synthesis of the Zn(II) complex: A solution of zinc(II) acetate dihydrate (2.34 mg, 0.110 mmol) in ethanol (2 mL) was added dropwise to a solution of H_3L (3.41 mg, 0.099 mmol) in tetrahydrofuran (2 mL) and acetonitrile (3 mL) at room temperature. The obtained transparent mixed solution

was allowed to stand at room temperature for about one month. The solvent was partially evaporated and several yellow block-shaped single crystals which suitable for X-ray crystallographic analysis were obtained.

X-Ray structure determination: The crystal data and structure refinement for the Zn(II) complex are given in Table-1. The single crystal of the Zn(II) complex with the approximate dimensions of 0.18 × 0.10 × 0.07 mm was placed on a Bruker Smart 1000 CCD area detector. The reflections were collected using a graphite monochromated MoK_α radition (λ = 0.71073 Å) at 298(2) K. The structure was solved by using the program SHELXL-97 and fourier difference techniques and refined by the full-matrix least-squares method on F^2. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE Zn(II) COMPLEX

Empirical formula	$C_{42}H_{48}N_4O_{18}Zn_4$
Formula weight	1158.32
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, °)	a = 9.9145(9), b = 10.7051(11), c = 12.1482(12) α = 8.234(2), β = 72.1540(10), γ = 74.0980(10)
Volume (Å^3)	1178.4(2)
Z, Calculated density (mg/m^3)	1, 1.632
Absorption coefficient (mm^{-1})	2.089
F(000)	592
Crystal size (mm)	0.18 × 0.10 × 0.07
Limiting indices	-11 ≤ h ≤ 11, -11 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected/unique	6015/4103 [$R_{(int)}$ = 0.2021]
Completeness to θ = 25.02	98.50 %
Data/restraints/parameters	4103/0/311
Goodness-of-fit on F^2	1.053
Final R indices [I > 2σ(I)]	R_1 = 0.0490, wR_2 = 0.1247
R indices (all data)	R_1 = 0.0766, wR_2 = 0.1699
Largest diff. peak and hole (e·Å^{-3})	0.996 and -1.276

RESULTS AND DISCUSSION

An new salamo-type bisoxime ligand H_3L and its Zn(II) complex have been synthesized. The composition are confirmed by elemental analyses and characterized by IR, UV-visible spectra and X-ray crystallography.

Composition of H_3L and Zn(II) complex: The colours, yields and elemental analytical results of H_3L and its Zn(II) complex are presented in Table-2. Their compositions agree with the formulae.

IR spectra of H_3L and its Zn(II) complex: The IR spectral data of H_3L and its corresponding Zn(II) complex are given in Table-3.

The characteristic C=N stretching band of the free ligand H_3L appears at 1620 cm^{-1}, while the C=N band of the Zn(II) complex is observed at 1610 cm^{-1}. The Ar-O stretching band occurs at 1258 cm^{-1} for H_3L, whereas at 1202 cm^{-1} for the Zn(II) complex. The shifts of C=N and Ar-O stretching frequencies indicate that the Zn-N and Zn-O bonds are formed between the Zn(II) ions and the oxime N and the phenolic O atoms of deprotonated L^{3-} unit. Meanwhile, a O-H stretching band of the free ligand H_3L at 3414 cm^{-1} disappears in its Zn(II) complex, indicating the oxygen atom in phenolic alcohol of the Zn(II) complex has been deprotonated and coordinated to the Zn(II) ions. In the 1582-1442 cm^{-1} region, the observed bands were attributed to aromatic C=C vibrations. In addition, the Zn(II) complex has one expected absorption band at 3415 cm^{-1}, assigned to hydroxyl group of two coordinated ethanol, indicating the existence of ethanol molecules in the Zn(II) complex, which is in agreement with the elemental analytical results of the Zn(II) complex.

UV-visible spectra of H_3L and its Zn(II) complex: The UV-visible spectra of H_3L and its corresponding Zn(II) complex in diluted CH_2Cl_2 solution are presented in Table-4. The UV-visible spectrum of the free ligand H_3L exhibits two absorption peaks at 272 and 324 nm. The former absorption peak at 272 nm can be assigned to the π-π^* transition of the benzene rings, while the latter one at 324 nm can be attributed to the intra-ligand π-π^* transition of the C=N bonds[17], which are characteristic of the Zn(II) complex with N_2O_2 coordination sphere[18,19].

Compared with the absorption peaks of the free ligand, the corresponding absorption peak at 291 nm is observed in the Zn(II) complex, which is bathochromically shifted by 19 nm and the Zn(II) complex has a MLCT at 363 nm, indicating that the oxime nitrogen atom is involved in coordination to the Zn(II) atom[20].

Structural description of Zn(II) complex: The molecular structure of the Zn(II) complex is shown in Fig. 1. Selected bond lengths and angles are listed in Table-5.

TABLE-2
COLOURS, YIELDS AND ANALYTICAL DATA OF H_3L AND ITS Zn(II) COMPLEX

Compound	m.f. (m.w.)	Colour	Yield (%)	Found (Calcd.) (%)			
				C	H	N	Zn
H_3L	$C_{17}H_{18}N_2O_6$ (346.33)	Brown	78.0	58.82 (58.96)	5.31 (5.24)	8.16 (8.09)	-
Complex	$C_{42}H_{48}N_4O_{18}Zn_4$ (1158.41)	Yellow	45.6	43.61 (43.55)	4.14 (4.18)	4.81 (4.84)	22.61 (22.58)

TABLE-3
IR SPECTRAL (cm^{-1}) DATA FOR H_3L AND ITS Zn(II) COMPLEX

Compound	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C)benzene ring skeleton
H_3L	1620	1258	3414	1582, 1494, 1473
Complex	1610	1202	3415	1535, 1461,1442

TABLE-4
UV-VISIBLE SPECTRA DATA OF H_3L AND ITS Zn(II) COMPLEX

Compound	C ($\times10^{-4}$ mol L^{-1})	First band		Second band	
		λ_{max1} (nm)	ε_1 ($\times10^4$ L mol^{-1} cm^{-1})	λ_{max2} (nm)	ε_2 ($\times10^4$ L mol^{-1} cm^{-1})
H_3L	6.00	272	2.27	324	2.70
Complex	3.00	291	4.85	363	6.05

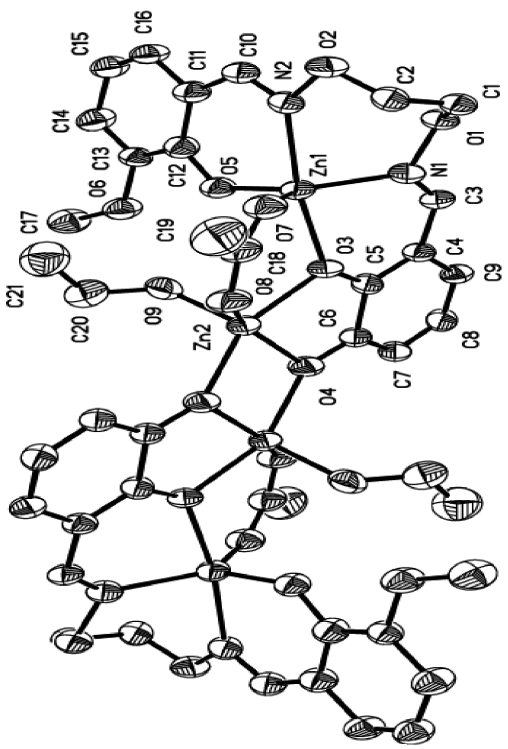

Fig. 1. Molecule structure and atom numberings of the Zn(II) complex

X-ray crystallographic analysis of the Zn(II) complex reveals formation of a tetranuclear structure. The Zn(II) complex crystallizes in the triclinic system, space group P-1 and Z = 1. The assembly of four Zn(II) atoms, two tridentate L^{3-} units, two acetate ions and two coordinated ethanol molecules result in the Zn(II) complex. In symmetric molecule unit of the Zn(II) complex, the Zn(II) (Zn1 or $Zn1^{\#1}$) ions are five-coordinated by N_2O_2 donors of deprotonated L^{3-} units and one oxygen atom of the acetate ion ($\tau = 0.773$). And the Zn(II) (Zn2 or $Zn2^{\#1}$) ions are also five-coordinated by three deprotonated phenoxo oxygen (O3, $O3^{\#1}$ and O4) atoms from two tridentate L^{3-} units, one oxygen atom of the coordinated ethanol molecule and one oxygen atom of the acetate ion ($\tau = 0.122$). One acetate ion serves as bidentate ligand for Zn2 and Zn1 and another one coordinates to $Zn2^{\#1}$ and $Zn1^{\#1}$ *via* Co-O-C-O-Co bridge, respectively. The Zn(II) atoms of the Zn(II) complex have slightly distorted tetragonal pyramidal geometry and pentahedral geometry, respectively. The coordination configuration of the Zn(II) complex is given in Fig. 2.

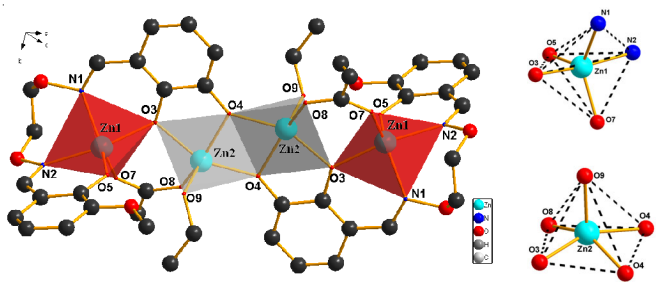

Fig. 2. Coordination configuration of $[(ZnL)_2(AcO)_2\{Zn(EtOH)\}_2]$

Supramolecular interactions of Zn(II) complex: The Zn(II) complex links other molecules into an infinite 2D supramolecular structure *via* hydrogen bond C(17)- H(17A)···$\pi_{centroid(C4-C9)}$ interactions and the weak C17-H17B···O2 interactions. As illustrated in Fig. 3 and Table-6, the monomers are linked by intermolecular C17-H17B···O2 and C1-H1A···O1 hydrogen bond interactions, C(17)-H(17A)···$\pi_{centroid(C4-C9)}$ interactions into an infinite 3D supramolecular structure.

TABLE-5
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE Zn(II) COMPLEX

Bond	Lengths	Bond	Lengths	Bond	Lengths
Zn(1)-O(5)	1.925(14)	$Zn(2)-O(4)^{\#1}$	2.032(14)	Zn(2)-O(4)	2.061(13)
Zn(1)-O(7)	1.989(17)	Zn(2)-O(9)	2.056(17)	Zn(2)-O(3)	2.073(13)
Zn(1)-O(3)	2.037(12)	Zn(1)-N(1)	2.072(18)	$O(4)-Zn(2)^{\#1}$	2.032(13)
Zn(1)-N(2)	2.125(17)	Zn(2)-O(8)	1.998(15)	-	-
Bond	Angles	Bond	Angles	Bond	Angles
O(5)-Zn(1)-O(7)	114.9(7)	$O(4)^{\#1}$-Zn(2)-O(9)	102.4(6)	C(5)-O(3)-Zn(2)	113.4(11)
O(5)-Zn(1)-O(3)	95.4(6)	O(8)-Zn(2)-O(4)	147.7(6)	Zn(1)-O(3)-Zn(2)	114.5(7)
O(7)-Zn(1)-O(3)	92.0(6)	$O(4)^{\#1}$-Zn(2)-O(4)	78.0(7)	$C(6)-O(4)-Zn(2)^{\#1}$	144.2(12)
O(5)-Zn(1)-N(1)	120.0(7)	O(9)-Zn(2)-O(4)	104.6(6)	C(6)-O(4)-Zn(2)	113.7(11)
O(7)-Zn(1)-N(1)	125.0(7)	O(8)-Zn(2)-O(3)	95.5(6)	$Zn(2)^{\#1}$-O(4)-Zn(2)	102.0(7)
O(3)-Zn(1)-N(1)	84.7(6)	O(9)-Zn(2)-O(3)	93.6(6)	C(12)-O(5)-Zn(1)	131.1(13)
O(5)-Zn(1)-N(2)	89.6(7)	O(4)-Zn(2)-O(3)	79.4(5)	C(18)-O(7)-Zn(1)	136.7(16)
O(7)-Zn(1)-N(2)	92.2(6)	C(3)-N(1)-Zn(1)	123.8(15)	C(18)-O(8)-Zn(2)	127.9(15)
O(3)-Zn(1)-N(2)	171.4(6)	O(1)-N(1)-Zn(1)	122.1(12)	C(20)-O(9)-Zn(2)	124.5(16)
N(1)-Zn(1)-N(2)	86.7(7)	C(10)-N(2)-Zn(1)	125.6(15)	$O(4)^{\#1}$-Zn(2)-O(3)	155.0(6)
$O(8)-Zn(2)-O(4)^{\#1}$	97.8(6)	O(2)-N(2)-Zn(1)	126.0(14)	-	-
O(8)-Zn(2)-O(9)	107.5(6)	C(5)-O(3)-Zn(1)	125.0(13)	-	-

Symmetry transformations used to generate equivalent atoms:$^{\#1}$ -x + 1, -y + 1, -z + 1

TABLE-6
MAIN INTERMOLECULAR HYDROGEN BONDS FOR Zn(II) COMPLEX

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠D-H···A
C(1)-H(1A)···O(1)	0.967	2.677	3.410(4)	132.95
C(17)-H(17B)···O(2)	0.955	2.614	3.481(5)	151.14
C(17)-H(17A)···$\pi_{centroid(C4-C9)}$	0.960	3.119	3.753(5)	124.95

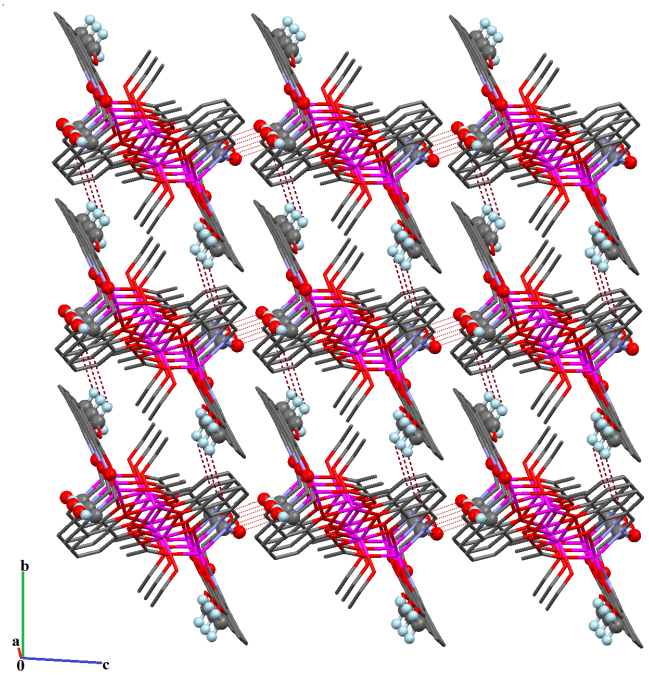

Fig. 3. 3D Supramolecular interactions of $[(ZnL)_2(AcO)_2\{Zn(EtOH)\}_2]$

Conclusion

A new salamo-type bisoxime ligand 6-methoxy-6'-hydroxy-2,2'-[ethylene-diyldioxy*bis*(nitrilomethylidyne)]-diphenol (H_3L) and its corresponding Zn(II) complex $[(ZnL)_2(AcO)_2\{Zn(EtOH)\}_2]$ have been synthesized and characterized by elemental analyses, IR spectra and UV-visible spectra *etc*. Meanwhile, the crystal and supramolecular structures of the Zn(II) complex were studied.

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