

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and **Biomolecular Spectroscopy**

journal homepage: www.elsevier.com/locate/saa



Synthesis, crystal structure and spectroscopic properties of a supramolecular zinc(II) complex with N₂O₂ coordination sphere



Wen-Kui Dong*, Li-Sha Zhang, Yin-Xia Sun, Meng-Meng Zhao, Gang Li, Xiu-Yan Dong

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, PR China

HIGHLIGHTS

- A halogen-substituted Salen-type bisoxime has been synthesized firstly.
- A new complex $[ZnL(H_2O)_2]_n$ has been synthesized and characterized structurally
- The complex forms a self-assembling infinite dual metal-water chain-like structure.
- Some new results are very important to coordination and supramolecular chemistry.

GRAPHICAL ABSTRACT

A new hexa-coordinated zinc(II) complex, namely $[ZnL(H_2O)_2]_n$, with N₂O₂ coordination sphere has been synthesized and structurally characterized structurally. The zinc(II) complex exhibits a slightly distorted octahedral geometry with halogen-substituted Salen-type bisoxime forming the basal N₂O₂ coordination sphere and two oxygen atoms from two coordinated water molecules in the axial position. The hydrogen-bonding and π - π stacking interactions have stabilized the zinc(II) complex molecules to form a selfassembling infinite dual metal-water chain-like structure with the nearest Zn...Zn distance of 4.954(4) Å.



ARTICLE INFO

Article history: Received 23 September 2013 Received in revised form 10 October 2013 Accepted 17 October 2013 Available online 5 November 2013

Keywords: Spectroscopic property

Salen-type bisoxime Zinc(II) complex Synthesis Supermolecular structure

ABSTRACT

A new hexa-coordinated zinc(II) complex, namely $[ZnL(H_2O)_2]_n$, with N₂O₂ coordination sphere $(H_2L = 4,4'-dibromo-6,6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol)$ has been synthesized and structurally characterized by elemental analyses, IR, UV-vis spectra and TG-DTA analyses, etc. Crystallographic data are monoclinic, space group $P2_1/c$, *a* = 24.634(2) Å, *b* = 10.144(1) Å, *c* = 7.9351(6) Å, β = 91.371(2)°, V = 1982.4(3) Å³, Dc = 2.099 g/cm³, *Z* = 4. The zinc(II) complex exhibits a slightly distorted octahedral geometry with halogen-substituted Salen-type bisoxime forming the basal N2O2 coordination sphere and two oxygen atoms from two coordinated water molecules in the axial position. The hydrogen-bonding and π - π stacking interactions have stabilized the zinc(II) complex molecules to form a self-assembling infinite dual metal-water chain-like structure with the nearest Zn...Zn distance of 4.954(4) Å.

© 2013 Elsevier B.V. All rights reserved.

Introduction

Supramolecular chemistry has recognized Salen-type complexes because of their involvement in π - π stacking interactions

* Corresponding author. Tel./fax: +86 931 4938703. E-mail address: dongwk@126.com (W.-K. Dong).

among chelate rings and the associated aromatic rings and/or intermolecular hydrogen-bonding interactions [1,2]. Supramolecular complexes have attracted intense attentions because of their unique applications such as heterogeneous catalysis, molecular adsorptions, and ion exchanges [3].

As one branch of supermolecular chemistry, Transition metal complexes bearing Salen-type ligand or its derivatives have been

^{1386-1425/\$ -} see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.saa.2013.10.072

of considerable current interest due to their ubiquitous use in a variety of catalytic chemical transformations, besides, Salen-type complexes offer both high reactivity and selectivity include epoxidation of olefins, asymmetric ring-opening of epoxides, olefin aziridination, olefin cyclopropanation and formation of cyclic and linear polycarbonates [4–6]. Moreover, the potential applications of Salen-type species, especially in the area of asymmetric catalysis for organic reactions [7], models of reaction centers of metalloenzymes [8], nonlinear optical materials [9] and building blocks for cyclic supramolecular structures [10] were gradually recognized on the basis of wide research work. And new materials can be produced by using these compounds, which seem to be suitable candidates for further chemical modifications [11-15]. In this paper, we report the synthesis, characterization, spectroscopic properties and supramolecular structures of a new hexa-coordinated zinc(II) complex $[ZnL(H_2O)_2]_n$ with halogen-substituted Salen-type bisoxime Ligand.

Experimental

Materials

3-Bromo-5-chloro-2-hydroxybenzaldehyde was purchased from Acros Organics and recrystallized from ethanol. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory.

Methods

The methods are the same as reported early [5–9].

Synthesis of the ligand H₂L

1,2-Bis(phthalimidoxy)ethane was prepared according to the literature [16]. Yield: 95.6%, m.p. 250 °C.

1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier [16]. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.97 (s, 4H), 5.52 (s, 4H).

4,4'-Dibromo-6,6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H₂L) was prepared by modification of the reported method [17]. To an ethanol solution (8 ml) of 3-bromo-5-chloro-2-hydroxybenzaldehyde (266.0 mg, 1.13 mmol) was added an ethanol solution (3 ml) of 1,2-bis(aminooxy)ethane (52.0 mg, 0.57 mmol), the color of the mixing solution turned to pale-yellow immediately. The mixture was stirred at 55 °C for 4 h. After cooling to room temperature, the precipitate was filtered, and washed successively with ethanol and ethanol/hexane (1:4), respectively. The product was dried under vacuum, and obtained 231.40 mg colorless solid. Yield: 77.7%. m.p. 202–204 °C. ¹H NMR (400 MHz, DMSO- d_6) δ : 4.49 (s, 4H), 7.57 (d, *J* = 2.4 Hz, 2H), 7.73 (d, *J* = 2.4 Hz, 2H), 8.84 (s, 2H), 10.40 (s, 2H). Anal. Calcd. for C₁₆H₁₂₋ Br₂Cl₂N₂O₄ (%): C, 36.47; H, 2.30; N, 5.32. Found: C, 36.69; H, 2.35; N, 5.10.

Synthesis of the zinc(II) complex $[ZnL(H_2O)_2]_n$

A solution of zinc(II) acetate dihydrate (219.50 mg, 1.0 mmol) in ethanol (10 ml) was added dropwise to a solution of H_2L (526.99 mg, 1.0 mmol) in acetone/acetonitrile (3/2, V/V) (20 ml) at room temperature. The color of the mixing solution turned to pale-yellow immediately, and the mixture was filtered and the filtrate was allowed to stand at room temperature for about four months, the solvent was partially evaporated and obtained pale-yellow prismatic single crystals suitable for X-ray crystallographic analysis. Yield: 36%. Anal. Calcd. for $C_{16}H_{14}Br_2Cl_2N_2O_6Zn$ (%): C,

30.68; H, 2.25; N, 4.47; Zn, 10.44. Found: C, 30.90; H, 2.11; N, 4.54; Zn, 10.26.

X-ray crystallography

The single crystal of the zinc(II) complex with the approximate dimensions of $0.49 \times 0.20 \times 0.17$ mm was selected on a Bruker Smart diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 298(2) K. The absorption corrections were carried out by the empirical method. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. The structure was solved by using the program SHEL-XS-97 [18] and Fourier difference techniques, and refined by fullmatrix least-squares method on F^2 using SHELXL-97 [19].

Details of the data collection and refinements of the zinc(II) complex are given in Table 1. The atomic coordinates and thermal parameters for all atoms are presented in Table 2.

Results and discussion

Molar conductances

The zinc(II) complex is soluble in THF, DMF, DMSO, but not soluble in acetone, ethanol, methanol and hexane. Molar conductance value of the zinc(II) complex at 25 °C of 10^{-3} mol dm⁻³ DMF solution is $5.8 \Omega^{-1}$ cm² mol⁻¹, indicating that the zinc(II) complex is non-electrolyte.

IR spectra

Table 1

F(000)

Crystal size (mm)

Limiting indices

Completeness to θ

Absorption correction

Refinement method

Goodness-of-fit on F²

R indices (all data)

Final *R* indices $[I > 2\sigma(I)]$

IR spectra of H₂L and its corresponding zinc(II) complex (Fig. 1) exhibit several distinguishable resonances in the 100–4000 cm⁻¹ region consistant with the coordination geometry revealed from structure determination.

The characteristic C=N stretching band of the free ligand H₂L appears at 1606 cm⁻¹, while the C=N band of the zinc(II) complex is observed at 1608 cm⁻¹. The shift of this C=N absorption by about 2 cm⁻¹ on going from the free ligand H₂L to the zinc(II)

Crystal data and structure refinement for the zinc(II) complex.					
Empirical formula	$C_{16}H_{14}Br_2Cl_2N_2O_6Zn$				
Formula weight	626.38				
Temperature (K)	298(2)				
Wavelength (Å)	0.71073				
Crystal system, space group	Monoclinic, $P2_1/c$				
Unit cell dimensions (Å, °)					
а	24.634(2)				
b	10.144(1)				
С	7.9351(6)				
	91.371(2)				
Volume (Å ³)	1982.4(3)				
7 Calculated density (Mg/m^3)	4				

5 5 7 8

1224

1.65-25.01

3486/0/262

1.000

 $0.49 \times 0.20 \times 0.17$

99.7% (θ = 25.01°)

0.9917 and 0.9592

0.526 and -0.611

9659/3486 [R_{int} = 0.0488]

 $R_1 = 0.0323, wR_2 = 0.0669$

 $R_1 = 0.0501 \ WR_2 = 0.0725$

 $-28 \le h \le 29, -7 \le k \le 12, -9 \le l \le 9$

Semi-empirical from equivalents

Full-matrix least-squares on F²

Absorption coefficient (mm⁻¹)

Reflections collected/unique

Max. and min. transmission

Data/restraints/parameters

Largest diff. peak and hole (e $Å^{-3}$)

Theta range for data collection (°)

Table 2

Atomic coordinate (×10⁴, ×10³ for H atoms) and thermal parameters U_{ec}/U_{iso} (Å², ×10³) in the zinc(II) complex.

Atom	x/a	y/b	z/c	$U_{\rm eq}/U_{\rm iso}$
Zn1	2436(1)	3962(1)	4714(1)	25(1)
Br1	1355(1)	-235(1)	4992(1)	37(1)
Br2	3640(1)	-11(1)	4652(1)	48(1)
Cl1	-361(1)	2659(1)	7336(1)	44(1)
Cl2	5342(1)	3138(1)	2796(2)	55(1)
N1	1764(1)	5332(3)	4597(3)	25(1)
N2	3054(1)	5412(3)	4822(3)	27(1)
01	1806(1)	6709(2)	4328(3)	35(1)
02	2934(1)	6715(2)	5395(3)	34(1)
03	1851(1)	2524(2)	4674(3)	27(1)
04	3076(1)	2631(2)	4892(3)	31(1)
05	2504(1)	3968(2)	2031(3)	29(1)
06	2406(1)	4139(2)	7434(3)	31(1)
C1	2232(1)	7003(3)	3176(4)	32(1)
C2	2724(2)	7535(3)	4078(5)	34(1)
C3	1294(2)	5078(3)	5153(4)	28(1)
C4	1078(1)	3785(3)	5542(4)	26(1)
C5	1358(1)	2583(3)	5225(4)	23(1)
C6	1049(1)	1430(3)	5510(4)	27(1)
C7	535(1)	1429(4)	6149(4)	32(1)
C8	290(1)	2628(4)	6512(5)	31(1)
C9	555(1)	3783(4)	6186(4)	31(1)
C10	3563(2)	5267(4)	4638(4)	33(1)
C11	3834(2)	4031(3)	4287(5)	30(1)
C12	3579(1)	2785(4)	4493(4)	27(1)
C13	3929(2)	1691(3)	4265(5)	31(1)
C14	4457(2)	1778(4)	3777(5)	40(1)
C15	4676(1)	3029(4)	3509(5)	38(1)
C16	4378(2)	4127(4)	3802(5)	39(1)



Fig. 1. Infrared spectra of H_2L and its corresponding zinc(II) complex. (a) H_2L ; (b) the zinc(II) complex.

complex suggest zinc(II) ions coordinate to the N atom of the C=N double bond.

The Ar—O stretching frequencies appear as a strong band within 1263–1213 cm⁻¹ range as reported for similar ligands [20]. These bands occur at 1251 cm⁻¹ for H_2L and at 1209 cm⁻¹ for the zinc(II)

complex, which is shifted to lower frequencies by ca. 42 cm⁻¹ upon complexation. This indicates the Zn–O bonds are formed between the zinc(II) ions and oxygen atoms of phenolic groups [21,22]. In addition, O–H stretching bands can be found at 3377 cm⁻¹ and the characteristics of the coordinated water absorption bands occur at 1639 and 505 cm⁻¹ in the zinc(II) complex, providing the evidence for existence of coordinated water molecules.

The far-infrared spectrum of the zinc(II) complex is obtained in the region of $500-100 \text{ cm}^{-1}$ in order to identify frequencies due to the Zn–O and Zn–N bonds. The IR spectrum of the zinc(II) complex shows vibrational absorption frequencies at 453 and 418 cm⁻¹, which are assigned to v(Zn–N) and v(Zn–O), respectively.

UV-vis absorption spectra

UV-vis absorption spectra of the free ligand H₂L and its corresponding zinc(II) complex in the diluted DMF solution at 298 K is shown in Fig. 2. The absorption spectrum of the free ligand H₂L shows an absorption peak at 273 nm. This is the characteristic absorption peak for any Salen-type ligands due to π - π * transitions of the benzene rings in the molecular structure [23,24]. It is of note that there is a broad absorption around 323 nm, which is seen in the corresponding Salen-type analogues. The absorption is ascribed to the keto-NH form of Salen-type compounds [25,26].

Compared with the absorption peak of the free ligand H₂L, the corresponding absorption peak of the zinc(II) complex observed at 279 nm, which is bathochromically shifted by ca. 6 nm, indicating the coordination of zinc(II) ion with deprotonated $(L)^{2-}$ unit. Meanwhile, the absorption peak at 323 nm disappears from the UV–vis spectrum of the zinc(II) complex, which indicates that the oxime nitrogen atom is involved in coordination to the metal atom. In addition, a new absorption peak is observed at 371 nm in the zinc(II) complex, which is assigned to an L \rightarrow M charge transfer transition. This is characteristic of a transition metal complex with N₂O₂ coordination sphere (Table 3) [27].

Thermal properties

The experimental results show that the thermal behavior of the free ligand H_2L is significantly different from those of the zinc(II) complex. The free ligand H_2L has a small sharp endothermic peak at 203 °C in DTA curve, with no weight loss in the TG curve, which is its melting point. On further heating, the free ligand H_2L has a



Fig. 2. UV-vis absorption spectra of H₂L and its corresponding zinc(II) complex.

H

Table 3	
UV-vis absorption spectra of H ₂ L and its Zn(II) complex in DMF (5.0 \times 10 ⁻⁵ mol L ⁻¹)	



Fig. 3. ORTEP drawing of the zinc(II) complex $[ZnL(H_2O)_2]_n$ with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

C1

C2

exothermic peak at 256 °C, with a gradual weight loss in the TG curve, and the free ligand decomposes completely by one step.

Thermal decomposition process of the zinc(II) complex can be mainly divided into two stages. The initial weight loss occurs in the range of 128–150 °C. The TG curve shows that the weight loss corresponding to this temperature range is 5.4% that roughly coincides with the value of 5.8%, calculated for the loss of two coordinated water molecules. The solid remains stable up to 340 °C and the second weight loss starts at around 345–369 °C with further

Table 4

Selected bond distances	(Å)	and	bond	angles	(°)	for	the	zinc(II)	complex
-------------------------	-----	-----	------	--------	-----	-----	-----	----------	---------

Table	5				
-------	---	--	--	--	--

Hydrogen bonding distances (.	(Å) and bond angles (°)	١.
-------------------------------	-------------------------	----

D—H···A	d(D—H)	d(H···A)	∠DHA	$d(D{\cdots}A)$
05–H5A···03	0.85	2.07	156	2.869(3)
05—H5B…04	0.85	2.02	144	2.759(3)
06-H6A04	0.85	2.46	133	3.098(4)
06—H6B···03	0.85	2.01	160	2.827(3)
O5—H5A…Br1	0.85	2.91	126	3.471(4)
O5—H5B…Br2	0.85	2.96	130	3.574(4)
O6—H6A…Br2	0.85	2.81	152	3.587(4)
O6—H6B…Br1	0.85	2.96	124	3.507(4)
C1—H1A· · · O2	0.97	2.68	108	3.120(3)
C1—H1A·…O1	0.97	2.58	151	3.461(4)
C2—H2A···O2	0.97	2.36	130	3.076(3)
C2—H2A···Br2	0.97	3.01	104	3.383(4)
C2−H2B···Br2	0.97	2.96	107	3.383(4)

decomposition of the zinc(II) complex. The TG curve shows around 84.7% total weight loss at 460 °C indicating the complete removal of organic part of the zinc(II) complex. The final product is likely ZnO with a residual value of 15.3% (theoretical residual value was 12.8%).

Crystal structures of $[ZnL(H_2O)_2]_n$

Single crystal X-ray diffraction determination reveals the structure of the zinc(II) complex is only built up by $[ZnL(H_2O)_2]$ units. The zinc(II) complex crystallizes in the monoclinic system, space group $P2_1/c$, and the unit cell contains four zinc(II) complex molecules. The monomeric octahedral unit of the structure are shown in Fig. 3. Selected bond lengths and angles are listed in Table 4.

The structure of $[ZnL(H_2O)_2]$ adopts a slightly distorted octahedral geometry with a hexa-coordinated zinc(II) center. The $(L)^{2-}$ unit of the zinc(II) complex behaves as a N₂O₂ tetradentate agent via two phenolic oxygen atoms and two oxime nitrogen atoms,

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1) - O(3)	2.051(2)	N(1) - O(1)	1.417(3)	C(5) - C(6)	1.417(5)
Zn(1) - O(4)	2.077(2)	N(2) - C(10)	1.273(4)	C(6) - C(7)	1.376(5)
Zn(1) - N(2)	2.117(3)	N(2) - O(2)	1.431(3)	C(7) - C(8)	1.390(5)
Zn(1) - O(5)	2.139(2)	O(1) - C(1)	1.439(4)	C(8) - C(9)	1.369(5)
Zn(1) - N(1)	2.163(3)	O(2)-C(2)	1423(4)	C(10)-C(11)	1.450(5)
Zn(1)-O(6)	2.168(2)	O(3)-C(5)	1.303(4)	C(11)-C(16)	1.407(5)
Br(1)-C(6)	1.898(3)	O(4)-C(12)	1.296(4)	C(11)-C(12)	1.422(5)
Br(2)—C(13)	1.896(3)	C(1)-C(2)	1.493(5)	C(12)-C(13)	1.420(5)
Cl(1)-C(8)	1.746(4)	C(3)-C(4)	1.452(5)	C(13)-C(14)	1.370(5)
Cl(2)-C(15)	1.754(4)	C(4)—C(9)	1.398(5)	C(14)-C(15)	1.397(5)
N(1)-C(3)	1.274(4)	C(4)—C(5)	1.426(5)	C(15)-C(16)	1.357(5)
Bond	Angles	Bond	Angles	Bond	Angles
O(3)-Zn(1)-O(4)	94.07(10)	C(5)-C(4)-C(3)	123.6(3)	C(9)—C(8)—C(7)	119.9(3)
O(3) - Zn(1) - N(2)	178.10(10)	O(3)-C(5)-C(6)	121.6(3)	C(9)-C(8)-Cl(1)	120.1(3)
O(4) - Zn(1) - N(2)	84.57(10)	O(3) - C(5) - C(4)	123.9(3)	C(7)-C(8)-Cl(1)	120.0(3)
O(3)-Zn(1)-O(5)	93.91(9)	C(6) - C(5) - C(4)	114.5(3)	C(8) - C(9) - C(4)	121.2(3)
O(4) - Zn(1) - O(5)	89.58(9)	C(7)-C(6)-C(5)	124.2(3)	N(2)-C(10)-C(11)	125.5(4)
N(2)-Zn(1)-O(5)	88.01(10)	C(7)-C(6)-Br(1)	117.0(3)	C(16)-C(11)-C(12)	121.3(3)
O(3) - Zn(1) - N(1)	85.32 (10)	C(5)-C(6)-Br(1)	118.8(3)	C(16)—C(11)—C(10)	116.0(3)
C(9) - C(4) - C(3)	115.2(3)	C(6)-C(7)-C(8)	119.0(3)	C(12)-C(11)-C(10)	116.0(3)
O(4) - C(12) - C(13)	121.6(3)	C(14)-C(13)-C(12)	124.7(3)	C(13)-C(14)-C(15)	118.3(4)
O(4) - C(12) - C(11)	124.2(3)	C(14)-C(13)-Br(2)	117.9(3)	C(16)—C(15)—C(14)	120.5(4)
C(13)-C(12)-C(11)	114.1(3)	C(12)-C(13)-Br(2)	117.4(3)	C(16)-C(15)-Cl(2)	121.2(3)
O(4) - Zn(1) - N(1)	178.44(10)	O(5) - Zn(1) - N(1)	91.89(9)	C(14)-C(15)-Cl(2)	118.3(3)
N(2) - Zn(1) - N(1)	96.01(11)	O(3) - Zn(1) - O(6)	91.90(9)	C(15)-C(16)-C(11)	120.8(4)
O(4) - Zn(1) - O(6)	91.76(9)	C(3) - N(1) - Zn(1)	123.8(2)	C(10) - N(2) - Zn(1)	128.6(3)
N(2)— $Zn(1)$ — $O(6)$	86.82(10)	O(1) - N(1) - Zn(1)	125.4(2)	O(2) - N(2) - Zn(1)	120.0(2)
C(3) - N(1) - O(1)	108.8(3)	C(10)—N(2)—O(2)	110.8(3)	N(1) - O(1) - C(1)	111.0(2)
C(2) - O(2) - N(2)	112.4(2)	C(12) - O(4) - Zn(1)	129.3(2)	O(2) - C(2) - C(1)	114.7(3)
C(5) - O(3) - Zn(1)	128.6(2)	O(1)-C(1)-C(2)	111.4(3)	N(1)-C(3)-C(4)	126.7(3)



Fig. 4. Projection of the infinite 2D supramolecular network of the zinc(II) complex onto the *ac* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

which are in the equatorial positions. The four N₂O₂ donor atoms of the (L)²⁻ unit are approximately coplanar, and the dihedral angle of N1–N2–O4 and N1–O3–O4 is about 0.12(2)°. The axial sites are occupied by two water molecules in a considerably large angle of 05-Zn1-O6 (174.51(9)°). It is noticeable that the bond distance Zn1–O5 (2.139(2)Å) is significantly shorter than Zn1–O6 (2.168(2) Å), which indicate the different coordination abilities of the two coordinated water molecules. The zinc(II) atom of the complex is nearly coplanar with the mean plane through the N_2O_2 core, deviating from the mean plane by 0.026(2) Å. Thus, the octahedral zinc(II) center contains a N2O2O2 coordination sphere made up of $(L)^{2-}$ unit in the equatorial plane and two coordinated water molecules in the axial position. The seven-membered chelate ring (Zn1-N1-O1-C1-C2-O2-N2) in the zinc(II) complex is a gauche conformation with the ethylene carbon atoms above the N_2O_2 coordination plane (C1, 1.292(2)Å and C2, 0.836(3) Å). The Zn–O (phenolic) bonds of 2.051(2) Å and 2.077(2) Å and Zn–N (oxime) bonds of 2.163(3) Å and 2.117(3) Å are in agreement with the average bond lengths seen for the corresponding bonds in the zinc(II) complexes bearing tetradentate Salen-type ligands in a planar fashion [5,28–32].

Supramolecular interaction

The introduction of two coordinated water molecules in the zinc(II) complex successfully leads to the assembly of the $[ZnL(H_2O)_2]$ monomeric units by intermolecular hydrogen bonds (Table 5). As illustrated in Fig. 4, four strong intermolecular hydrogen bonds, O5—H5A···O3, O5—H5B···O4, O6—H6A···O4, and O6—H6B···O3, are formed between the four —OH groups of two coordinated water molecules and the two phenolic oxygen (O3 and O4) atoms of $(L)^{2-}$ units in two adjacent molecules, respectively.



Fig. 5. Projection of the infinite 2D supramolecular network of the zinc(II) complex onto the *bc* plane (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity).

Simultaneously, this linkage is further stabilized by four weaker intermolecular hydrogen bonds $O5-H5A\cdots Br1$, $O5-H5B\cdots Br2$, $O6-H6A\cdots Br2$ and $O6-H6B\cdots Br1$ with each hydroxyl group of the two coordinated water molecules hydrogen-bonded to two substituent Br atoms of $(L)^{2-}$ units of each adjacent molecule, respectively. Furthermore, it is noteworthy that the angle of the nearest benzene rings is $2.25(2)^{\circ}$ for C4-C9 ring and $1.98(2)^{\circ}$ for C11-C16 ring, and the distance between the neighboring benzene ring centroid for C4-C9 ring is 3.973(4)Å and 4.052(4)Å for C11-C16 ring, indicating weak π - π stacking interactions. Consequently, these hydrogen-bonding and π - π stacking interactions have stabilized the zinc(II) complex molecules to form a self-assembling infinite dual metal-water chain-like supramolecular structure with the nearest Zn…Zn distance of 4.954(4)Å [33,34].

In addition, the adjacent chains are further held together to form an infinite 2D-layer supramolecular structure by five pairs of intermolecular C1—H1A···O1, C1—H1A···O2, C2—H2A···O2, C2—H2A···Br2 and C2—H2B···Br2 hydrogen bonding interactions (Fig. 5). The methylene —C1H1A groups of the O-alkyl chain are hydrogen bonded to both oxime oxygen (O1 and O2) atoms of (L)^{2–} units of the adjacent molecule, respectively. Whereas, the methylene —C2H2A groups are hydrogen bonded to one oxime oxygen (O2) atom of the adjacent molecules and the substituent (Br2) atoms of (L)^{2–} units of the other adjacent molecules, respectively. Moreover, the —C2H2B groups are bonded to the same substituent (Br2) atoms, too [35,36].

Conclusions

Based on the data, description and discussion above, a new zinc(II) complex, $[ZnL(H_2O)_2]_n$, has been synthesized with a Salamotype chelating ligand 4,4'-dibromo-6,6'-dichloro-2,2'-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H₂L) in ethanol/acetone/ acetonitrile mixed solution, and characterized by elemental analyses, IR spectra, UV–vis absorption spectra, TG-DTA analyses, molar conductance measurement and X-ray Crystallography. In IR spectrum of the zinc(II) complex, the v(Zn–N) and v(Zn–O) vibrational absorption frequencies at 453 and 418 cm⁻¹ respectively were observed. The absorption bands were found at 3377, 1639 and 505 cm⁻¹, implying existence of coordinated water molecules. The X-ray crystal structure of the zinc(II) complex reveals that it is an asymmetric mononuclear structure and has a slight distortion toward octahedral geometry.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21361015), the Fundamental Research Funds for the Gansu Province Universities (212086) and the science and technology support funds of Lanzhou Jiaotong University (ZC2012003), which are gratefully acknowledged.

Appendix A. Supplementary material

Crystallographic data for the zinc(II) complex has been deposited with the Cambridge Crystallographic Data Center, CCDC No.: 696148, and can be free downloaded from the site www.ccdc. cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http:// dx.doi.org/10.1016/j.saa.2013.10.072.

References

- [1] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189–214.
- [2] M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor, L. Randaccio, J. Am. Chem. Soc. 106 (1984) 4478–4485.
- [3] P.G. Lacroix, Eur. J. Inorg. Chem. (2001) 339–348.
- [4] A.K. Sharma, F. Lloret, R. Mukherjee, Inorg. Chem. 46 (2007) 5128-5130.
- [5] W.K. Dong, J.G. Duan, G.L. Liu, Transit. Met. Chem. 32 (2007) 702-705.
- [6] W.K. Dong, C.E. Zhu, H.L. Wu, Y.J. Ding, T.Z. Yu, Synth. React. Inorg. Met.Org. Nano Met. Chem. 37 (2007) 61–65.
- [7] W.K. Dong, J. Yao, Y.X. Sun, L. Li, J.C. Wu, React. Inorg. Met.-Org. Nano-Met. Chem. 40 (2010) 521–528.
- [8] W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi, C.Y. Zhao, Inorg. Chim. Acta 362 (2009) 1129–1134.
- [9] W.K. Dong, X.N. He, H.B. Yan, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao, X.L. Tang, Polyhedron 28 (2009) 1419–1428.
- [10] M. Kondo, K. Nabari, T. Horiba, Y. Irie, M.K. Kabir, R.P. Sarker, E. Shimizu, Y. Shimizu, Y. Fuwa, Inorg. Chem. Commun. 6 (2003) 154–156.
- [11] A.Y. Robin, K.M. Fromm, Coord. Chem. Rev. 250 (2006) 2127-2157.
- [12] M. Kondo, M. Miyazawa, Y. Irie, R. Shinagawa, T. Horiba, A. Nakamura, T. Naito, K. Maeda, S. Utsuno, F. Uchida, Chem. Commun. (2002) 2156–2157.
- [13] J. Kim, B. Chen, T.M. Reineke, H. Li, M. Eddaoudi, D.B. Moler, M. O'Keeffe, O.M.
- Yaghi, J. Am. Chem. Soc. 123 (2001) 8239-8247.
- [14] W.K. Dong, Y.J. Ding, Cryst. Res. Technol. 43 (2008) 321–326.
- [15] W.K. Dong, J.Y. Shi, J.K. Zhong, Y.X. Sun, J.G. Duan, Struct. Chem. 19 (2008) 95– 99.
- [16] D.W. Dixon, R.H. Weiss, J. Org. Chem. 49 (1984) 4487-4494.
- [17] W.K. Dong, J.Y. Shi, L. Xu, J.K. Zhong, J.G. Duan, Y.P. Zhang, Appl. Organometal. Chem. 22 (2008) 89–96.
- [18] G.M. Sheldrick, SHELXS97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- [19] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [20] G.C. Percy, D.A. Thornton, J. Inorg. Nucl. Chem. 35 (1973) 2319-2327.
- [21] G.A. Kohawole, K.S. Patel, J. Chem. Soc., Dalton Trans. (1981) 1241–1253.
- [22] M. Asadi, K.A. Jamshid, A.H. Kyanfar, Inorg. Chim. Acta 360 (2007) 1725-1730.
- [23] S. Akine, T. Taniguchi, T. Nabeshima, Chem. Lett. (2001) 682-683.
- [24] Z.L. Chu, W. Huang, J. Mol. Struct. 837 (2007) 15-22.
- [25] S. Akine, T. Taniguchi, W.K. Dong, T. Nabeshima, J. Org. Chem. 70 (2005) 1704– 1711.
- [26] H.E. Smith, Chem. Rev. 83 (1983) 359–377.
- [27] L. Gomes, E. Pereira, B. Castro de, J. Chem. Soc., Dalton Trans. (2000) 1373– 1379.
- [28] W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He, X.L. Tang, Inorg. Chim. Acta 362 (2009) 117–124.
- [29] S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima, J. Am. Chem. Soc. 127 (2005) 540–541.
 - [30] S. Akine, T. Taniguchi, T. Nabeshima, Inorg. Chem. 43 (2004) 6142–6144.
 - [31] S. Akine, T. Taniguchi, T. Nabeshima, Chem. Lett. 35 (2006) 604–605.
 - [32] S. Akine, T. Hotate, T. Matsumoto, T. Nabeshima, Chem. Commun. 47 (2011) 2925–2927.
 - [33] H.L. Wu, X.C. Huang, J.K. Yuan, F. Kou, F. Jia, B. Liu, Y. Bai, Z. Naturforsch. 66b (2011) 1049–1055.
 - [34] H.L. Wu, F. Jia, B. Liu, J.K. Yuan, Y. Bai, Transit. Met. Chem. 36 (2011) 847–853.
 [35] S.S. Sun, C.L. Stern, S.T. Nguyen, J.T. Hupp, J. Am. Chem. Soc. 126 (2004) 6314–
 - 6326.
 [36] T.Z. Yu, K. Zhang, Y.L. Zhao, C.H. Yang, H. Zhang, L. Qian, D.W. Fan, W.K. Dong, L.L. Chen, Y.Q. Qiuet, Inorg. Chim. Acta 361 (2008) 233–240.