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Journal of Molecular Structure 654 (2003) 235-243

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# Synthesis, crystal structure and properties of the zinc complexes with unsymmetrical tridentate ligands

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Received 10 May 2002; revised 30 March 2003; accepted 1 April 2003

### Abstract

Two complexes of zinc (II) with mixed-ligand,  $[Zn_2(phen)_2(HL^1)_2]$  (ClO<sub>4</sub>)<sub>2</sub> (1) and  $[Zn_2(phen)_2(HL^2)_2]$  (ClO<sub>4</sub>)<sub>2</sub>(2) (H<sub>2</sub>L<sup>1</sup>=N-(2-hydroxybenzyl) ethanolamine and H<sub>2</sub>L<sup>2</sup> = N-(2-hydroxybenzyl) propanolamine), and another zinc complex ZnL<sup>1</sup> (3) were synthesized and characterized by elemental analysis, IR spectra, thermal analysis, fluorescence and <sup>1</sup>H NMR. The crystal structure of (1) has a centrosymmetric di-phenoxo-bridged dizinc (II) core and each zinc center is laid in a slightly distorted trigonal bipyramidal geometry. A 2D supramolecular structure is formed approximately along *bc* plane in terms of the action of multiple N-H···O and O-H···O hydrogen bonds between the (HL<sup>1</sup>)<sup>-</sup> ligands and the  $\pi$ ··· $\pi$  stacking interactions between the phenanthroline ligands. Thermal behavior, studied by TG and DTA in nitrogen atmosphere, indicates that phen is eliminated at higher temperature than (HL<sup>1</sup>)<sup>-</sup> and (HL<sup>2</sup>)<sup>-</sup>. Several possible mechanisms for the fluorescence quenching of the metal complexes are proposed.

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*Keywords:* Dinuclear zinc complex; Crystal structure; 2D supramolecular structure; Hydrogen bonds;  $\pi \cdots \pi$  Stacking interactions; Thermal analysis

### 1. Introduction

Zn complexes [1-6] have attracted increasing interest in the field of synthetic and biological chemistry particularly due to the key role they play in biological systems. Binuclear zinc coordination moieties are found in various zinc enzymes such as phosphatase [7-9] and metallo- $\beta$ -lactamases [10]. Although the detailed mechanism of these zinc enzymes in biological systems is not clear, one aspect has been confirmed, i.e. the coordination environments of the zinc (II) atoms such as the distance between two zinc cores are crucial to allow the cooperation of both zinc centers in the active sites [4]. A variety of model compounds for binuclear zinccontaining enzymes have been designed and synthesized to understand their biological functions [7-10].

To assemble 1D, 2D or 3D supramolecular structures has become another interesting area in coordination chemistry. Two important types of

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noncovalent interactions for building supramolecular networks, hydrogen bonds and aromatic  $\pi \cdots \pi$ stacking interactions, have recently attracted much more attention [11–15], for example, the supramolecular assemblies of zinc complexes involving the above two noncovalent interactions [16–19]. The supramolecular structures of some complexes containing fluorophores and some specific metal ions are expected to apply as sensing and switching devices through spectral changes [20].

Tridentate ligands  $H_2L^1 \cdot HC1$  and  $H_2L^2$  have demonstrated to be promising in the construction of the supramolecular networks connected by multiple hydrogen bonds [21]. On the other hand, phen has the potential applications to build the supramolecular structures via  $\pi \cdots \pi$  stacking interactions [22] and to prepare the efficient chemosensors due to the intensive emission and the binding sites of two amine groups [23].

Thus, the mixed-ligand Zn complexes containing the tridentate ligand and phen may give some supramolecular structures with interesting fluorescent properties.

Herein, we describe the studies of the syntheses, IR, <sup>1</sup>H NMR, fluorescence and thermal analysis of two zinc complexes with mixed-ligand,  $[Zn_2(HL^1)_2(-phen)_2](ClO_4)_2$  (1),  $[Zn_2(HL^2)_2(phen)_2](ClO_4)_2$  (2)  $(H_2L^1=N-(2-hydroxybenzyl)$  ethanolamine and  $H_2L^2=N-(2-hydroxybenzyl)$  propanolamine) and another zinc complex ZnL<sup>1</sup> (3). The synthesis of ZnL<sup>2</sup> was unsuccessful. For a better understanding, the properties of the Zn complex Zn(phen)\_3(ClO\_4)\_2 (4) [24] and free ligands  $H_2L^1$ -HCl and  $H_2L^2$  are also reported.

It is interesting that complex (1) can be selfassembled into a 2D supramolecular structure via the intermolecular hydrogen bonds between the  $(HL^1)^$ ligands and  $\pi \cdots \pi$  interactions between the phenanthroline rings.

# 2. Experimental

## 2.1. Materials and physical measurements

 $H_2L^1 \cdot HCl$ ,  $H_2L^2$  (Fig. 1) and complex (4) were prepared by the methods reported earlier [21,25,24].



Fig. 1. Structures of ligands  $H_2L^1$ ·HCl and  $H_2L^2$ .

 $Zn(ClO_4)_2 \cdot 6H_2O$  and phen  $\cdot H_2O$  were used as received without further purification.

IR spectra were recorded on a Bruker Vector-22 Spectrometer (KBr Disc.). Fluorescence spectra were measured with 850 Hitachi Fluorescence Spectrophotometer. Thermal analysis (TG, DTA) measurements were performed using Rigaku Thermoflex Thermal Analyzer in a flowing nitrogen atmosphere with heating rate of 10 °C min<sup>-1</sup>. A sample size of 2– 10 mg was used. The <sup>1</sup>H NMR measurements were carried out on a Bruker 300 Ultrashield NMR Spectrometer in DMSO-d<sup>6</sup>.

2.2. Preparation of  $[Zn_2(HL^1)_2(phen)_2](ClO_4)_2$  (1),  $[Zn_2(HL^2)_2(phen)_2](ClO_4)_2$  (2),  $ZnL^1$  (3) and  $Zn(phen)_3(ClO_4)_2$  (4)

Preparation of  $[Zn_2(HL^1)_2(phen)_2](ClO_4)_2$  (1). To a stirred methanol solution of H<sub>2</sub>L<sup>1</sup>·HCl (0.0814 g, 0.4 mmol), Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1490 g, 0.4 mmol) and phen·H<sub>2</sub>O (0.0793 g, 0.4 mmol) were added followed by the addition of an aqueous solution of NaOH (0.4 M, 0.1 ml, 0.4 mmol). The resulting solution was allowed to reflux for 4 h, then concentrated in vacuo, and the light yellowcoloured solid was collected by filtration, washed with methanol and dried. Yield: 0.16 g, 80%. Anal. Calcd for C42H40Cl2N6O12Zn2: C, 49.34; H, 3.94; N, 8.22%. Found: C, 49.02; H, 4.15; N, 8.09%. The filtrate was left undisturbed at room temperature for a few days affording light yellow-coloured crystals of (1) suitable for X-ray structural determination.

Synthesis of (2) is similar to that of (1). Yield: 0.18 g, 85%. Anal. Calcd for  $C_{44}H_{44}Cl_2N_6O_{12}Zn_2$ : C, 50.31; H, 4.22; N, 8.00%. Found C, 49.98; H, 4.25; N, 8.17%.

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*Preparation of* (3). To a stirred methanol solution of  $H_2L^{1}$ ·HCl (0.0814 g, 0.4 mol),  $Zn(ClO_4)_2$ ·6H<sub>2</sub>O (0.0814 g, 0.4 mmol) were added followed by the addition of NaOH (0.4 M, 0.1 ml, 0.4 mmol). The resulting solution was allowed to reflux for 4 h, then concentrated in vacuo, and the colourless solid was collected by filtration, washed with methanol and dried. Yield: 0.075 g, 82%. Anal. Calcd for C<sub>9</sub>H<sub>11</sub>N<sub>1</sub>O<sub>2</sub>Zn: C, 46.96; H, 4.82; N, 6.09%. Found: C, 46.49; H, 4.92; N, 5.94%.

# 2.3. X-ray data collection and structural determination

A single crystal of (1) was mounted on a glass-fiber. All measurements were made on a Rigaku RAXIS-IV image plate area detector with graphite monochromated Mo K $\alpha$  radiation. The data were collected at 18 °C and corrected for Lorentz and polarization effects. The correction for secondary extinction was applied. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms

#### Table 1

Crystal data and structure refinement for (1)

were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ( $I > 2.00\sigma(I)$ ) and variable parameters. All calculations were performed using SHELX-97 software package [26].

Crystallographic data for (1) are listed in Table 1.

# 3. Result and discussion

# 3.1. IR spectra

IR spectra, showing the characteristic absorptions of the complexes and the ligands are listed in Table 2. Two characteristic absorptions at 1421 and 853 cm<sup>-1</sup> for free phen, slightly shift to higher and lower frequencies, respectively, in the complexes. The strong unresolved broad band at 1050–1101 cm<sup>-1</sup> and the sharp band at  $624 \text{ cm}^{-1}$  are assigned to the vibrations of free  $ClO_4^-$ . The  $\mu_2$ -bridging mode of the phenoxo groups in (1) can be inferred from the

Empirical formula	$C_{21}H_{20}ClN_3O_6Zn$	
Formula weight	511.22	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	TRICLINIC, P-1	
Unit cell dimensions	a = 9.910(2)  Å	$\alpha = 110.63(3)$ (°)
	b = 11.330(2)  Å	$\beta = 108.55(3)$ (°)
	c = 11.529(2)  Å	$\gamma = 101.33(3)$ (°)
Volume	$1076.7(4) \text{ Å}^3$	
Z, Calculated density	2, 1.577 Mg/m <sup>3</sup>	
Absorption coefficient	$1.309 \text{ mm}^{-1}$	
F(000)	524	
Crystal size	$0.26 \times 0.25 \times 0.20 \text{ mm}$	
$\theta$ Range for data collection	2.05–27.54 (°)	
Index ranges	$-12 \le h \le 11, -14 \le k \le 13, 0 \le l \le 14$	
Reflections collected/unique	3786/3786	
Completeness to $2? = 27.54$	88.76%	
Max. and min. transmission	0.7798 and 0.7272	
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	3786/0/302	
Goodness-of-fit on $F^2$	1.029	
Final <i>R</i> indices $[I > 2\sigma(I)]$	R1 = 0.0771, wR2 = 0.1973	
R indices (all data)	R1 = 0.0997, wR2 = 0.2123	
Extinction coefficient	0.010(4)	
Largest diff. peak and hole	0.946 and $-0.987 \text{ e} \text{ \AA}^{-3}$	

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Table 2

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Characteristic IR spectral data for Zn complexes and ligands

Compounds	$\nu$ (N–H)	$\nu(Ar-O)$	Ring vibration	<i>ν</i> (C–H)	Vibration( $ClO_4^-$ )
(1)	3250(m)	1264(m)	1625(w), 1593(w), 1519(m), 1481(m), 1427(s), 850(s), 771(m), 726(s)	2925(w)	1090(s), 624(s)
(2)	3250(w)	1267(s)	1624(w), 1595(w), 1520(w), 1482(s)1429(m), 849(m), 770(s), 727(s)	2939(w)	1101(s), 624(m)
( <b>3</b> ) ( <b>4</b> ) Phen⋅H <sub>2</sub> O	3264(m)	1274(s)	1597(s), 1482(s), 760(s) 1627(m), 1588(m), 1523(s), 1430(vs), 849(s), 726(s) 1590(m), 1503(s), 1421(s), 853(s), 738(s)	2922(m), 2859(m)	1050(s), 623(s)
$H_2L^1 \cdot HCl$ $H_2L^2$	3198(s) 1237(s)	1257(s)	1592(s), 1458(s), 1439(s), 763(s) 1610(m), 1581(m), 1492(s), 762(s)	2965(m), 2839(m) 2970(m), 2862(m)	

 $\nu$ (C–O) vibration band at 1264 cm<sup>-1</sup>, which is lower than 1296 cm<sup>-1</sup>, responsible for the nonbridging mode in [Cu(HL<sup>1</sup>)<sub>2</sub>] [21]. For (**2**), the corresponding vibration bands are very alike, as the similar structure to (**1**).

# 3.2. Thermal analysis

Thermal behavior of the Zn complexes and the free ligands was studied by TG and DTA. The thermal analytical data are listed in Table 3. The complex (1) starts decomposition at 256 °C and then undergoes three stages of mass loss. In the first stage, the elimination of  $(HL)^-$  begins at 256 °C and ends at 505 °C, in which one strong exothermic peak at 360 °C and two small rapid mass losses in the TG curve can be observed. The second stage between 505 and 600 °C is assigned to the

Table 3 Thermal analytical data for Zn complexes and free ligands

decomposition of ClO<sub>4</sub><sup>-</sup>. Compared to the first stage, the loss rate of the second stage is relatively moderate. The removal of ligand phen ought to be completed in the third stage between 600 and 730 °C, in which there is a very steep mass loss. A continuous weight loss, owing to the removal of metallic zinc, occurs above 730 °C, much lower than the temperature reported for  $[Zn(sac)_2(ea)_2]$  [27]. Thermal analytical data in Table 3 show that ligand phen exhibits higher stability than ligand  $(HL^1)^-$  and  $ClO_4^-$  anion, as the initial decomposition temperatures are taken as a measure of thermal stability. However, at very high temperature, the exothermic elimination feature of phen can considerably speed up its-self decomposition. For complex (2), the decomposition takes place at 251 °C and also undergoes whole exothermic decomposition in three stages corresponding to the elimination of  $(HL^2)^{-}$ ,

Complexes	Stages	Temperature range (°C)	DTA <sub>max</sub> (°C) <sup>a</sup>	Mass los	ss (%)	Total ma (%)	ass loss	Solid residue
				Found	Calcd	Found	Calcd	
(1)	1	256-505	360(-)	30.4	32.5			
	2	505 - 600	520(-)	17.8	19.5			
	3	600-730	675(-)	37.2	35.3	85.4	87.3	Zn
(2)	1	251-570	275(-) 324(-) 510(-)		35.5	34.3		
	2	570-633	608(-)	19.7	19.0			
	3	633-750	709(-)	34.5	34.3	89.7	87.6	Zn
(3)	1	100-630	350(-) $495(-)$ $570(-)$	72.9	71.7	27.1	28.3	Zn
H <sub>2</sub> L <sup>1</sup> ·HCl	1	80-240	120(+)	18.5	17.9			
-	2	240-710	585(-)	81.2	82.1	99.7	100	None
$H_2L^2$	1	96-686	155(+) 184(+) 241(+) 677(+)	98.4	100	98.4	100	None

<sup>a</sup> (+), Endothermic; (-), exothermic.

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#### Table 4

Spectroscopic data of Zn complexes and ligands: wavelength of fluorescence maximum  $\lambda_{\rm F}$ /nm, wavelength of excitation  $\lambda_{\rm ex}$ /nm, emission intensity *F* 

Complexes (or ligands)	$\lambda_{ m F}$	$\lambda_{\mathrm{ex}}$	F
(1)	560	306	0.39
(2)	556	294	0.26
(3)	333 <sup>a</sup>	271	5.1
(4)	387	310	5.2
$H_2L^1 \cdot HCl$	319	262.5	10
$H_2L^2$	319	271.5	15.6

<sup>a</sup> An additional band appeared at 430 nm with F of 1.8 and overlapped with the 333 nm band.

ClO<sub>4</sub><sup>-</sup> and phen sequentially. Comparing the thermal decomposition temperatures for ligand phen in (1) (600 °C) and (2) (633 °C) with those reported for free phen (432 °C) [28] and phen coordinated in [Zn(H<sub>2</sub>. O)<sub>4</sub>(phen)](NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (ca. 320 °C) [29], we can draw a conclusion that ligand phen have higher thermal stability in (1) and (2).

For free ligand  $H_2L^1 \cdot HCl$ , the thermal decomposition consists of two stages. The first endothermic stage, can be reasonably assigned to the elimination of HCl, while the second one is the decomposition of  $H_2L^1$ . Unlike  $H_2L^1 \cdot HCl$  and other Zn complexes, ligand  $H_2L^2$  displays several unexpected endothermic peaks in the DTA curve. As shown in Table 3, free ligands  $H_2L^1 \cdot HCl$  and  $H_2L^2$  complete their decomposition above 710 and 686 °C, respectively.

# 3.3. Fluorescence of binuclear Zn complexes (1), (2) and mononuclear Zn complexes (3), (4)

The excitation, emission wavelength and emission intensity of the Zn complexes and the ligands are

collected in Table 4. It is known that phenolic derivatives, heterocyclic derivatives possess the fluorescence and the formation of metal chelates commonly promotes the fluorescence by strengthening rigidity and minimizing internal vibrations [30]. Generally, metal cation Zn can give rise to complexes' exhibiting fluorescence emission [31]. As expected, all Zn complexes in Table 4 show red-shift features, compared to free ligands  $H_2L^1 \cdot HCl$ ,  $H_2L^2$ and phen [32]. However, when the ligands coordinate to metal ion  $Zn^{2+}$ , we can see obvious puzzling fluorescence quenching. This may be explained as following: first, the CHEF (chelation-enhanced fluorescence) effect follows the order  $H^+ > Zn^{2+}$  [33], i.e. the Zn complexes of the ligands are less emissive than the protonated ligands. This explanation should be only suitable for  $H_2L^1 \cdot HCl$ , not for  $H_2L^2$ , because  $H_2L^2$  is not protonated; second, the chelated metal Zn ion is proximate to the chromophores  $(HL^{1})^{-}$  and  $(HL^2)^{-}$ , which can result in fluorescence quenching [34]. In other words, the coordination of Zn to phenoxo O and ethanolamine N may make it closer to the phenoxo and ethanolamine, so that the energytransfer between them, takes place easier. Third, although  $Zn^{2+}$  with  $d^{10}$ , has not any the charge transfer, its linking to phen and  $(HL^{1})^{-}$  (or  $(HL^{2})^{-}$ ) fragments may result in electron transfer between ligands in binuclear Zn complexes (1) and (2), and then the fluorescence quenching [35]. Finally, the considerably weak emission intensity of (1) and (2) may be also attributed to the steric constraint between the rigid phen ligands and  $(HL^{1})^{-}$  (or  $(HL^{2})^{-}$ ), which strengthens the vibronic interaction-induced quenching [36]. Obviously, the above explanations, except the first one, are related to the conformation of

Table 5

<sup>1</sup>H NMR spectra data ( $\delta$ , in ppm) for the ligands and the complexes

Compounds	Phenyl protons	Phen protons	Aliphatic protons
(1)	6.40-6.98	8.07-9.20	2.62(C2-H), 3.85(C1-H), 4.27(C3-H)
(2)	6.39-6.98	8.07-9.10	1.63(C3' – H), 2.70(C2' – H), 3.80(C1' – H), 4.48(C4' – H)
(3)	6.49-7.00		2.72(C2-H), 3.82(C1-H), 4.26(C3-H)
H <sub>2</sub> L <sup>1</sup> ·HCl	7.5-8.0		3.11(C2-H), 4.19(C1-H), 3.79(C3-H)
$H_2L^2$	6.78-7.24		2.15(C3'-H), 2.9(2'), 3.5(C1'-H), 3.86(C4'-H
Phen [37]		7.88-9.26	
$Zn(phen)_{3}^{2+}$ [38]		7.62-8.84	

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Fig. 2. View of complex (1) showing the numbering scheme at the 20% probability level with the H atoms omitted for clarity.

complexes. As shown in Table 4, the spectroscopic data of binuclear Zn complexes (1) and (2) are very close, possibly due to the similar structures of two complexes.

# 3.4. <sup>1</sup>*H* NMR spectra of $H_2L^1 \cdot HCl$ , $H_2L^2$ and their Zn complexes (1), (2), and (3)

<sup>1</sup>H NMR spectral data of the free ligands and the zinc complexes are listed in Table 5. Upon the complexiation of Zn (II) ion, <sup>1</sup>H NMR signals of

Table 6					
Selected bond	lengths	(Å) and	angles (	°) for	(1)

phenyl protons of ligands  $(HL^1)^-$  and  $(HL^2)^-$  and also the signals of C1 and C2 protons shift upfield, but downfield for C3 proton. For  $(HL^2)^-$ , the situation becomes more complicated, i.e. the signals of C-2' and C-3' protons shift upfield, while C-1' and C-4' protons exhibit signals downfield. A doublelet of (**3**) in the 6.49–7.00 range, can be assigned as phenyl protons (C<sub>6</sub>H<sub>4</sub>, 4H), which have higher  $\delta$  values in literature [**39**]. It is interesting that <sup>1</sup>H NMR spectra of (**1**) show a triplelet in the 6.40–6.98 range. This may be associated with the diphenxo-bridged complexation mode of (**1**). Contrary to those of the phenyl protons, <sup>1</sup>H NMR signals of the coordinated phen shift a little downfield as its coordination (Table 5).

# 3.5. Description of the structure (1)

A perspective view of complex (1) shows the atom numbering scheme in Fig. 2. Selected bond lengths and bond angles are listed in Table 6. Two zinc metal centers are both pentacoordinated and bridged by two phenoxo O atoms, resulting in a centrosymmetric structure. For each zinc (II) core, the Addison distortion index  $\tau$  [40] is 0.807 ( $\tau = 0$  for a square pyramid, and  $\tau = 1$  for a trigonal bipyramid), which suggests that the coordination geometry is a slightly distorted trigonal bipyramid. The axial positions (for Zn1) are occupied by N3 from phen and O (1)#1 from another (HL<sup>1</sup>)<sup>-</sup>, and the equatorial positions are occupied by N1, N2, O1 from another (HL<sup>1</sup>)<sup>-</sup>, phen and (HL<sup>1</sup>)<sup>-</sup>, respectively. Unlike phenoxo O atom, the alkoxyl O atom is left uncoordinated. The coplanar

Zn(1)-O(1)	1.967(4)	Zn(1)-N(3)	2.170(5)
Zn(1) - Zn(1)#1	3.1365(2)	O(1)-Zn(1)#1	2.123(4)
Zn(1) - N(1)	2.055(5)	Zn(1) - N(2)	2.089(5)
Zn(1)-O(1)#1	2.123(4)		
O(1) - Zn(1) - N(1)	122.63(2)	O(1) - Zn(1) - N(2)	117.31(2)
N(1)-Zn(1)-N(2)	119.6(2)	O(1)-Zn(1)-O(1)#1	79.94(2)
N(1)-Zn(1)-O(1)#1	90.25(2)	N(2)-Zn(1)-O(1)#1	92.97(2)
O(1) - Zn(1) - N(3)	105.08(2)	N(1)-Zn(1)-N(3)	93.1(2)
N(2)-Zn(1)-N(3)	78.2(2)	O(1)#1-Zn(1)-N(3)	171.06(2)
O(1)-Zn(1)-Zn(1)#1	41.79(1)	N(1)-Zn(1)-Zn(1)#1	109.95(2)
N(2)-Zn(1)-Zn(1)#1	108.84(1)	N(3)-Zn(1)-Zn(1)#1	146.28(2)
O(1)#1-Zn(1)-Zn(1)#1	38.14(1)		

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 2, -z + 2.

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Table 7 Hydrogen-bonds for (1) (Å and °)

D–H	d (H···A)	∠DHA	d (D···A)	A[symmetry operations]
N1–H1F O2–H2A N1–H1F O2–H2A	2.263 1.979 2.263 1.979	145.17 167.38 145.17 167.38	2.910 2.785 2.910 2.785	O6 $[1 - x, 3 - y, 2 - z]$ O5 $[1 - x, 3 - y, 2 - z]$ O6 $[x, 1 + y, 1 + z]$ O5 $[x, 1 + y, 1 + z]$

structure of N1, N2, O1, Zn1 can be evidenced by the sum of three neighboring angles  $(359.5(6)^\circ)$ : N1–Zn1–O1, N1–Zn1–N2, N2–Zn1–O1. The average Zn1–O bond length for Zn1–phenolate is 2.045(4) Å, comparable to the corresponding value of the complex  $[Zn_2(C_{25}H_{17}N_2O_2PS)_2Cl_2]$  (2.050(5) Å) [41]. The Zn1···Zn (1)#1 separation of 3.137 Å is almost equal to the value [Zn···Zn 3.13 Å] reported for

diphenoxo-bridged Zn complexes [42], but longer than the corresponding value [Zn···Zn 3.0540(18) Å] [43] and shorter than that [Zn···Zn 3.443(3) Å] of phenoxy-bridged binuclear Zn complex where the other bridging ligand is benzoato O atom [44]. Each Zn (1) and Zn (1)#1 are shown to be laid approximately in the coordinated phen mean planes.

A prominent feature of the complex (1) is the formation of 2D supramolecular network. Along *bc* plane, each complex molecule is surrounded by four such molecules. Approximately along *c* axis, there exist multiple hydrogen bonds between N–H, O–H groups of  $(HL^{1})^{-}$  ligands and perchlorate anions (Table 7), i.e. N1–H1F and uncoordinated O2–H2A groups act as hydrogen donors; the perchlorate anions act as hydrogen acceptors. Along *b* axis, the distance between two phen mean planes of adjacent molecules is approximately 3.5 Å, indicating that



Fig. 3. 2D supramolecular network of complex (1) approximately along the bc plane.



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the neighboring molecules are connected via  $\pi \cdots \pi$ interactions. From above discussion, it can be concluded that (1) was self-assembled into a 2D supramolecular structure approximately along *bc* plane via intermolecular N-H···O and O-H···O hydrogen bonds and  $\pi \cdots \pi$  stacking interactions between the phenanthroline rings (Fig. 3).

In conclusion, two mixed-ligand zinc (II) complexes  $[Zn_2(phen)_2(HL^1)_2]$  (ClO<sub>4</sub>)<sub>2</sub> (1) and  $[Zn_2(-phen)_2(HL^2)_2]$  (ClO<sub>4</sub>)<sub>2</sub> (2) and another zinc (II) complex (3) have been synthesized. Crystal structure of (1) reveals that it has a centrosymmetric structure with two zinc atoms bridged by two phenoxo O atoms. It is interesting for (1) to assemble into a 2D ordered supramolecular structure via hydrogen bonds and  $\pi \cdots \pi$  stacking interactions. Complex (2) has a similar structure to (1), based on the IR, thermal, <sup>1</sup>H NMR and fluorescence studies. Compared to (HL<sup>1</sup>)<sup>-</sup> and (HL<sup>2</sup>)<sup>-</sup>, phen displays better thermal stability. The possible mechanisms concerning fluorescence quenching have been proposed.

# Acknowledgements

This work was financially supported by the National Science Foundation of China (No. 30270321) and the Natural Science Foundation of Anhui Province (No. 01045408).

# References

- [1] A. Abufarag, H. Vahrenkamp, Inorg. Chem. 34 (1995) 2207.
- [2] T.H. Lu, K. Panneerselvam, S.F. Tung, T.Y. Chi, C.S. Chung, Acta Crystallogr. C53 (1997) 1780.
- [3] C. Flassbeck, K. Wieghardt, E. Bill, C. Butzlaff, A.X. Trautwein, B. Nuber, J. Weiss, Inorg. Chem. 31 (1992) 21.
- [4] P. Dapporto, M. Formica, V. Fusi, L. Giorgi, M. Micheloni, P. Paoli, R. Pontellini, P. Rossi, Inorg. Chem. 40 (2001) 6186.
- [5] T. Hökelek, H. Necefoğlu, Acta Crystallogr C52 (1996) 1128.
- [6] M.L. Godino-Salido, M.D. Gutiérrez-Valero, R. López-Garzón, J.M. Moreno-Sánchez, Inorg. Chim. Acta 221 (1994) 177.
- [7] K.J. Abe, J. Izumi, M. Ohba, T. Yokoyama, H. Ōkawa, Bull. Chem. Soc. Jpn 74 (2001) 85.
- [8] E. Kimura, I. Nakamura, T. Koike, M. Shionoya, Y. Kodoma, T. Ikeda, M. Shiro, J. Am. Chem. Soc. 116 (1994) 4764.
- [9] T. Kioke, M. Inoue, E. Kimura, M. Shiro, J. Am. Chem. Soc. 118 (1996) 3091.

- [10] N.V. Kaminskaia, B. Spingler, S.J. Lippard, J. Am. Chem. Soc. 122 (2000) 6411.
- [11] J. Tercero, C. Diaz, M.E. Fallah, J. Ribas, X. Solans, M.A. Maestro, J. Mahia, Inorg. Chem. 40 (2001) 3077.
- [12] B.Q. Ma, S. Gao, H.L. Sun, G.X. Xu, Crystengcomm 35 (2001) U1.
- [13] Y.Q. Zheng, J.L. Liu, J. Sun, Z. Anorg. Allg. Chem. 627 (2001) 1997.
- [14] J.L. Liu, Y.Q. Zheng, Z.P. Kon, H.L. Zhang, Z. Anorg. Allg. Chem. 627 (2001) 1066.
- [15] Y.S. Xie, H. Jiang, M.G. Yu, C.X. Du, Q.L. Liu, X.L. Xu, Y. Zhu, J. Mol. Struct. 608 (2002) 169.
- [16] A.D. Burrows, R.W. Harrington, M.F. Mahon, C.E. Price, J. Chem. Soc., Dalton Trans. 21 (2000) 3845.
- [17] H.K. Liu, J. Hu, T.W. Wang, X.L. Yu, J. Liu, B.S. Kang, J. Chem. Soc., Dalton Trans. 23 (2001) 3534.
- [18] N. Yoshida, K. Ichikawa, M. Shiro, J. Chem. Soc., Perkin Trans. 2 (2000) 17.
- [19] H.G. Zhu, M. Ströbele, Z. Yu, Z. Wang, H.J. Meyer, X.Z. You, Inorg. Chem. Commun. 4 (2001) 577.
- [20] M.B. Inoue, F. Medrano, M. Inoue, A. Raitsimring, Q. Fernando, Inorg. Chem. 36 (1997) 2335.
- [21] Y.S. Xie, W.M. Bu, A.S.C. Chan, X.L. Xu, Q.L. Liu, Z.D. Zhang, Y.G. Fan, Inorg. Chim. Acta 310 (2000) 257.
- [22] R.F. Klevtsova, L.A. Glinskaya, S.M. Zemskova, S.V. Larionov, Polyhedron 18 (1999) 3559.
- [23] A. Bencini, M.A. Bernardo, A. Bianchi, V. Fusi, C. Giorgi, F. Pian, B. Valtancoli, Eur. J. Inorg. Chem. (1999) 1911.
- [24] A.A. Schilt, R.C. Taylor, J. Inorg. Nucl. Chem. 9 (1959) 211.
- [25] Y.S. Xie, W.M. Bu, X.L. Xu, H. Jiang, Q.L. Liu, Y. Xue, Y.G. Fan, Inorg. Chem. Commun. 4 (2001) 558.
- [26] G.M. Sheldrick, SHELX97, Program for Crystal Structure Refinement, University of Göttigen, Germany, 1997.
- [27] V.T. Yilmaz, Y. Topcu, F. Yilmaz, C. Thoene, Polyhedron 20 (2001) 3209.
- [28] I.B. Johns, E.A. Mcelhill, J.O. Smith, J. Chem. Engng Data 7 (1962) 277.
- [29] C.G. Zhang, C. Janiak, J. Chem. Cryst. 31 (2001) 29.
- [30] A.D. Naik, S.M. Annigeri, U.B. Gangadharmath, V.K. Revankar, V.B. Mahale, Spectrochim. Acta, Part A 58 (2002) 1713.
- [31] S. Alves, F. Pina, M.T. Albelda, E.G. España, C. Soriano, S.V. Luis, Eur. J. Inorg. Chem. (2001) 405.
- [32] S. Ikeda, S. Kimachi, T. Azumi, J. Phys. Chem. 100 (1996) 10528.
- [33] M.A. Bernardo, F. Pina, E.G. España, J. Latorre, S.V. Luis, J.M. Llinares, J.A. Ramírez, C. Soriano, Inorg. Chem. 37 (1998) 3935.
- [34] G. Klein, D. Kaufmann, S. Schürch, J.L. Reymond, Chem. Commun. (2001) 561.
- [35] G.D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Taglietti, Angew. Chem. Int. Ed. Engl. 35 (1996) 202.
- [36] M.B. Inoue, I.C. Muñoz, M. Inoue, Q. Fernando, Inorg. Chim. Acta 300–302 (2000) 206.
- [37] J.D. Miller, R.H. Prince, J. Chem. Soc. (1965) 4706.
- [38] J.D. Miller, R.H. Prince, J. Chem. Soc. (1965) 3185.

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- [39] M. Shakir, O.S.M. Nasman, S.P. Varkey, Polyhedron 15 (1996) 309.
- [40] A.W. Addison, T.N. Rao, J. Reedijk, J. Van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
- [41] P.P. Lourido, J. Romero, J.A.G. Vázquez, A. Sousa, C.A. McAuliffe, M. Helliwell, Inorg. Chim. Acta 279 (1998) 249.
- [42] H. Adams, D. Bradshaw, D.E. Fenton, Inorg. Chem. Commun. 5 (2002) 12.
- [43] H. Adams, D. Bradshaw, D.E. Fenton, Eur. J. Inorg. Chem. (2001) 859.
- [44] S. Uhlenbrock, B. Krebs, Angew. Chem., Int. Ed. Engl. 31 (1992) 1647.
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