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Two novel tetranuclear zinc(II) clusters with different topological structures: Crystal structures and luminescence properties

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ABSTRACT

Two novel tetranuclear zinc(II) clusters with different topological structures have been synthesized by using $Zn(ClO_4)_2 \cdot 6H_2O$, sodium azide and potentially multidentate Schiff base ligands containing different substituent groups. The two complexes have been characterized by elemental analysis, IR, single crystal X-ray diffraction and fluorescence studies. Structural studies reveal that $[Zn_4(HL^1)_4(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**1**) is a linear tetranuclear cluster whereas $[Zn_4(HL^2)_4(\mu_{1,1}\text{-}N_3)_4]$ (**2**) is a square-planar tetranuclear cluster. Both two complexes display intraligand ($\pi \rightarrow \pi^*$) fluorescence. Due to the heavy atom effect which increases the probability for intersystem crossing to the triplet state, the fluorescence intensity of complex **2** is much lower than that of complex **1**.

In recent years diverse supramolecular architectures have emerged not only because they have potential applications in various fields [1–4], but also for considerable progresses that have been achieved in the rational design and preparation of interesting coordination compounds. In addition, a lot of papers have reported the design of the various ligands that can control the interesting structures of complexes to some extent [5,6]. For the same type of ligands, different substituents in the ligands may also lead to some unexpected results [7,8]. Among various ligands, the Schiff base ligands have been investigated extensively by scientists [9,10]. Not only because they can serve easily coordinated N and O atoms but also because they possess many straightforward synthetic pathways. By changing the species of aldehydes and alcohols, various Schiff base ligands with different substituents can be obtained. Followed by this, a variety of metal-cluster structures can be obtained [11,12]. In this paper, H_2L^1 (2-((2-hydroxypropylimino)-methyl)-phenol) and H_2L^2 (2-((2-hydroxypropylimino)-methyl)-4-Br-phenol) (see Scheme 1) have been prepared successfully based on our deliberate design [13].

Zn(II) ion has no optical spectroscopic characteristic due to its closed-shell $3d^{10}$ configuration, however it can strengthen the luminescence of the ligand after coordination with ligand [14]. So the zinc Schiff base complexes with variegate fluorescence properties have attracted much attention due to their potential applications in biological systems [15], photophysical properties [16,17] and in emitting materials of organic light emitting diodes [18].

In this work, we have successfully synthesized two novel zinc(II) tetranuclear complexes containing Schiff base ligands that have different substituents. Our strategy is to control the topological structures of clusters by changing the substituents within Schiff base ligands. Because of the subtle difference in the Schiff base ligands, linear and square-planar tetranuclear Zn(II) complexes, $[Zn_4(HL^1)_4(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**1**) [19] and $[Zn_4(HL^2)_4(\mu_{1,1}\text{-}N_3)_4]$ (**2**) [20] have been obtained, respectively. The fluorescence properties of complexes **1** and **2** have also been studied.

Single-crystal X-ray diffraction analyses [21] (Crystal data for the complexes **1** and **2** are shown in Table S1) reveal that complex **1** is a linear tetranuclear cluster which can be viewed as a phenoxy-bridged $[Zn_2(HL^1)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ dimer. The asymmetric unit consists of two Zn(II) ions, two $(HL^1)^-$ anions, and two N_3^- anions. A perspective view of the tetranuclear structure is illustrated in Fig. 1. And some selected bond lengths and angles are presented in Table S2. All Zn(II) ions adopt highly distorted tetragonal pyramid coordination spheres. The Zn1 shows a N_2O_3 donor set including two μ_2-$O_{phenoxy}$ $(HL^1)^-$, $O_{protonated\text{-}alkoxo}$ $(HL^1)^-$, and N_{amine} $(HL^1)^-$ all in the equatorial positions and N (EO-N_3^-) in the apical position. The coordination environment of the Zn2 possesses a N_3O_2 donor set including $O_{phenoxy}$ $(HL^1)^-$, $O_{protonated\text{-}alkoxo}$ $(HL^1)^-$, N_{amine} $(HL^1)^-$, and N (EO-N_3^-) all in the equatorial positions and N (N_3^-) in the apical position. Zn1 and Zn2 are bridged through one EO-N_3^- generating a $[Zn_2(HL^1)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ unit with Zn···Zn distance 3.698(2) Å. The Zn1–N6–Zn2 angle is 126.1(4)°. In complex **1**, the Zn – O bond lengths vary from 2.007(5) Å to 2.187(6) Å and the Zn – N bond lengths vary from 1.995(8) Å to 2.076(7) Å.

It is interesting that the two such $[Zn_2(HL^1)_2(\mu_{1,1}\text{-}N_3)(N_3)]$ units are linked through double deprotonated phenolate oxygen atoms to give a novel linear tetranuclear Zn(II) cluster and to form a Zn_2O_2 subunit in the tetranuclear structure. The Zn···Zn distance within the Zn_2O_2 subunit is 3.151(2) Å falling in the normal range (2.94–3.24 Å) reported in some literatures [22–25].

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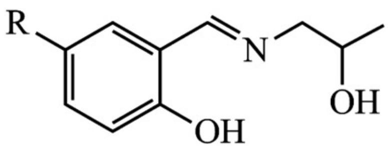

H_2L^1: R = H

H_2L^2: R = Br

Scheme 1. Structural diagram of the Schiff base ligands.

The crystal structure of complex **2** indicates that **2** is composed of four Zn(II) ions, four $(HL^2)^-$ and four EO-N_3^-. Actually, the asymmetric unit of complex **2** consists of one Zn(II) ion, one $(HL^2)^-$ and one N_3^-. A perspective view of the tetranuclear structure is illustrated in Fig. 2. And some selected bond lengths and angles are presented in Table S3. The zinc(II) ion adopts distorted trigonal-dipyramidal coordination spheres and is arranged at the corners of a square. Zn1 is pentacoordinated with a N_3O_2 donor set including two N (EO-N_3^-), N_{amine} $(HL^1)^-$, $O_{phenoxy}$ $(HL^1)^-$ and $O_{protonated\text{-}alkoxo}$ $(HL^1)^-$, which reveals a distorted trigonal-dipyramidal coordination sphere with the equatorial-planar Zn – N bonds and the axial Zn – O bonds. The four symmetry-related Zn(II) centers connected by four EO-azide nitrogen atoms construct an interesting tetranuclear structure. Furthermore, the Zn ions and EO-azide nitrogen atoms construct an eight-membered ring in which the EO-azide nitrogen atoms occupy the alternating position: below and above the plane defined by four Zn ions. In this eight-membered ring, angles at nitrogen and zinc are 131.9(5)° and 113.6(5)°, respectively. The neighboring Zn(II)···Zn(II) distance is 3.660(2) Å. The Zn(II)···Zn(II) distance along the catercorner of the square is 5.162(2) Å. All the Zn – N bond lengths vary from 1.991(1) Å to 2.034(8) Å and the Zn – O bond lengths are 2.018 (8) Å and 2.259(8) Å, respectively.

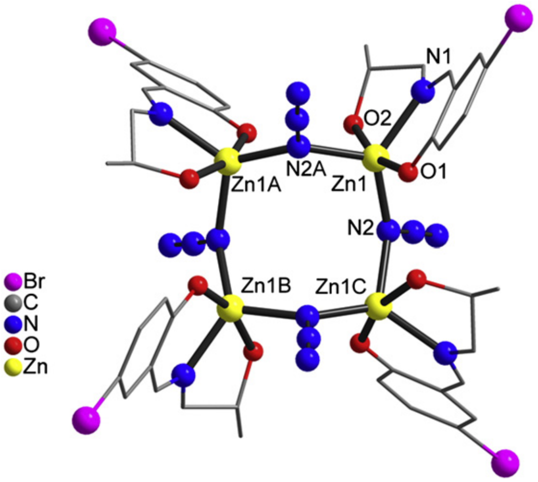

Fig. 2. A perspective view of structure for $[Zn_4(HL^2)_4(\mu_{1,1}\text{-}N_3)_4]$ (**2**). Hydrogen atoms are omitted for clarity. Symmetry codes: (A) −y, x, −z; (B) −x, −y, z; (C) y, −x, −z.

Complexes **1** and **2** are prepared under the identical experimental conditions except the use of different Schiff-base ligands. Reaction of $Zn(ClO_4)_2\cdot 6H_2O$, H_2L^1 and NaN_3 in MeOH/EtOH/H_2O yields **1**. Replacement of H_2L^1 with H_2L^2 in the above reaction affords **2**. Compared with H_2L^1, the presence of the electron-withdrawing group (– Br) instead of H atom in H_2L^2 increases the steric hindrance effect [26]. Therefore, this subtle difference of substituents in Schiff-base ligands results in a linear tetranuclear cluster and a square-planar tetranuclear cluster, respectively (see Scheme 2).

An unprecedented atom connectivity, $Zn(EO\text{-}N_3)Zn(\mu_2\text{-}O)_2Zn(EO\text{-}N_3)Zn$, is found in complex **1**. The external Zn ions link to internal Zn ions via an EO-N bridge. The internal Zn ions are connected by two μ_2-$O_{phenoxy}$ atoms. Thus the linear $[Zn_4O_2N_2]$ core is constructed. This linear core contained in **1** (see Scheme 2) is the first example in Zn(II) complexes. However, the linear structure of similar geometries is discovered in some papers in which O atoms instead of N atoms form the linear shape [27,28]. In addition, the existence of Zn–(EO-N_3)–Zn moieties in **2** forms a $[Zn_4N_4]$ core. The Zn···Zn distance bridged by EO-N_3 is 3.660(2) Å, which indicates the four Zn ions that construct a square. To the best of our knowledge, this is the first example of $[Zn_4N_4]$ cluster with a square topology presenting EO-N_3 bridges.

Complexes **1** and **2** both exhibit various structures and reveal potential different fluorescence properties, so the fluorescence properties of two Zn(II) complexes were investigated at room temperature (298 K) in solid state (Fig. 3). Complexes **1** and **2** show the fluorescence spectra centered on 466 and 490 nm respectively. In terms of d^{10} configuration of Zn(II) complexes based on Schiff ligands, the emission is tentatively assigned to the π → π* intraligand fluorescence [29]. The fluorescence

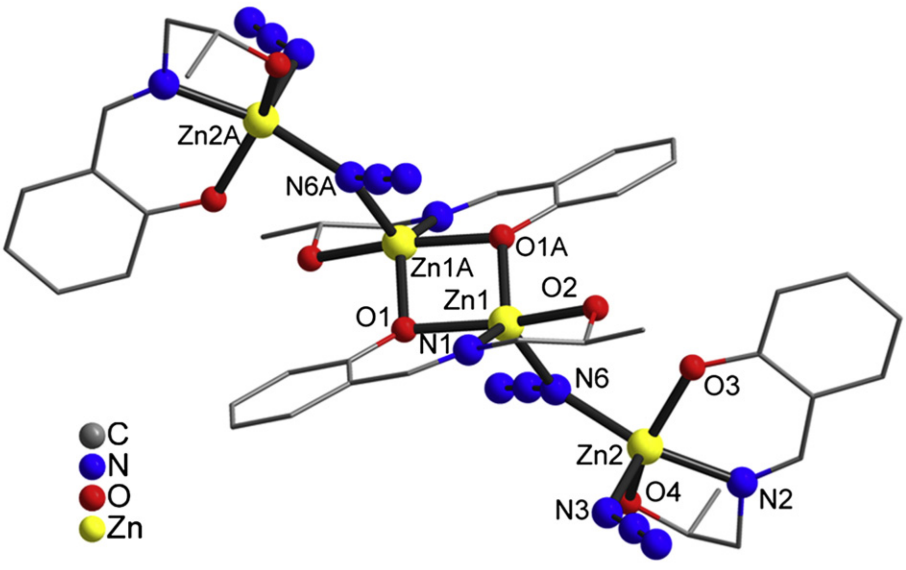

Fig. 1. A perspective view of structure for $[Zn_4(HL^1)_4(\mu_{1,1}\text{-}N_3)_2(N_3)_2]$ (**1**). Hydrogen atoms are omitted for clarity. Symmetry codes: 1 − x, 1 − y, 1 − z.