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Synthesis, crystal structures and luminescent properties of tetranuclear Zn molecular clusters with aroylhydrazone ligand[†]

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Two kinds of tetranuclear Zn(II) molecular clusters with the designed aroylhydrazone Schiff base ligand (H_3L) , $[Zn_4(HL)_4]$ · 3(DMF)·3(H₂O) (1) and $[Zn_4(HL)_2(CH_3COO)_4]\cdot2(DMF)\cdot2(CH_3OH)$ (2), have been synthesized and studied. Molecular cluster 1 displayed a Zn₄O₄ boat-shaped core and 2 presented a discrete linear tetranuclear Zn(II) structure. The luminescent properties of the two molecular clusters have been investigated, which exhibit a wide range of photo-luminescence in different organic solvents.

Introduction

Molecular clusters have received a significant amount of attention for their structural diversity resulting from their metal-rich nature and chemical stability combined with their fascinating potential application in advanced materials.¹⁻³ An increasing number of geometrically intriguing molecular clusters, for example, linear,⁴ olive,⁵ wheel,⁶ helical,⁷ cubane, rectangular, chair and boat conformations, have been successfully obtained. The structures of molecular clusters are dependent upon the chemical structures of the ligand, metal ions, anions, pH value, metal-to-ligand ratio and solvents.^{1-3,8} The most important factor among these that controls molecular clusters are ligands with suitably disposed bridging groups. Generally, there are two main classes of ligands: one is ligands with appended potentially endogenous bridging groups linking metal ions in a closed-cluster system (e.g. cubane, rectangular, chair, boat cluster);⁸ the other is large ligands with arrays of coordination pockets suitably organized to create specific geometric arrangements of metal centres through bridging connections, which can be assembled with metal ions in an open-cluster (e.g. linear).4 The employment of auxiliary ligands is often applied in the construction of molecular clusters combining the two classes of ligands above.⁹

We have designed and synthesized an aroylhydrazone Schiff base ligand.¹⁰ A preliminary study of its transition metal complexes and a few related literature reports¹¹ have indicated that this kind of ligand possesses the advantage of constructing polynuclear complexes. To extend our research, another aroylhydrazone Schiff base ligand, (E)-N'-(2,3-dihydroxybenzylidene)-4hydroxybenzohydrazide (H₃L), was designed and synthesized (Scheme 1). On comparison with the ligand in our previous work,¹⁰ an additional hydroxyl group was introduced at the 3-position of the benzylidene part, which provided suitable, disposable bridging groups to control the stereochemistry of the metallic centres as well as the number of metal ions within the cluster motifs. Two kinds of tetranuclear Zn(II) molecular clusters have been constructed by this ligand successfully. Interestingly, complex 1 is the first example of a supramolecular diamondoid structure with a boat-shaped tetranuclear molecular cluster as its node.

Results and discussion

Synthesis

As shown in Scheme S2, ESI,[†] the H_3L ligands in both molecular clusters are HL^{2-} anions, in which the two hydroxyl groups of the 2,3-dihydroxybenzaldehyde part are deprotonated. In the synthesis of **1**, sodium hydroxide is necessary to deprotonate the hydroxyl



Scheme 1 Structural formula for (E)-N'-(2,3-dihydroxybenzylidene)-4-hydroxybenzohydrazide, H_3L .

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group of the ligand, while in the corresponding reaction of the synthesis of **2**, it is not necessary to add a base since zinc acetate is used instead of the zinc perchlorate in **1**. Clearly, the acetate is a ditopic ligand that can act as a base and a bridging ligand at the same time. Inspired by the different synthesis conditions, **1** and **2** are both tetranuclear Zn clusters. Therefore, the supply of an excess hydroxyl substitute on the ligand H_3L is an effective strategy to construct molecular clusters. Meanwhile, the ratio of M : L, the pH value and the auxiliary ligand play an important role in controlling the structures of the molecular clusters in this work. The ligation of hydroxyl groups in the HL^{2-} ligand has different coordination modes in **1** and **2** (Scheme S3, ESI†), which gives a distinctive core structure of **1** and **2**.

Crystal structure of 1

The reaction of $Zn(ClO_4)_2 \cdot 6H_2O$ with H_3L (1 : 1 molar ratio) in DMF-CH₃OH-H₂O (1:3:2 volume ratio) in the presence of NaOH produces yellow crystals of [Zn₄(HL)₄]·3(DMF)·3(H₂O) (1) in a 65% yield, the molecular structure of which was determined by single-crystal X-ray diffraction, as depicted in Fig. 1a. The molecular cluster 1 crystallizes in the tetragonal space group $P\bar{4}$. The coordination geometry of the Zn(II) centre is a distorted squared-based pyramid ($\tau = 0.23$).¹² Each ligand coordinates to a Zn atom with the imine-nitrogen, carbonyl-oxygen and phenoxooxygen atom and bridges a neighbouring Zn atom through its phenolate group (μ_2 -O1). The HL²⁻ ligands display the $\eta^1:\eta^2:\eta^1:\eta^1:\mu_2$ chelating-bridging mode, as shown in Scheme S3a, ESI.[†] Four ligands link four Zn(II) centres to form an eightmembered ring which is folded in a boat conformation (Fig. S2, ESI[†]). Thus, 1 is an unusual tetranuclear cluster with a boatshaped Zn₄O₄ core having two pairs of parallel ligand strands arranged in a head-to-tail fashion. To best of our knowledge, this is the second example of a boat tetranuclear cluster,^{8e} while most of the clusters are rectangular or cube-core structures.8 The peripheral O-M-O angles are ca. 105.1° and 111.7°, therefore the overall arrangement of the $[Zn_4(HL)_4]$ unit is close to tetrahedral geometry (Fig. S3a, ESI[†]). The Zn…Zn separations in 1 are 3.4534(11) and 3.7167(2) Å, respectively. Taking the hydrogenbonding function of H_3L into account, $[Zn_4(HL)_4]$ is a selfcomplementary moiety in which the uncoordinated oxygen atoms in the terminal -OH groups in the ligands form strong H-bonding with coordinated -OH groups from an adjacent moiety (Fig. 2a and 2b). These moieties are self-assembled through the H-bonding into a 3D diamondoid network (Fig. 2c). It was noted that many diamondoid networks of coordination complexes are

(a) (b) C12 C13 C13 C13 C14 C15 C15 C14 C15 C14 C15 C14 C15 C15 C14 C15 C14 C15 C14 C15 C14 C

Fig. 1 View of the coordination environments of Zn and the ligands in (a) 1 and (b) 2. Solvent molecules and hydrogen atoms are omitted for clarity.



Fig. 2 (a) The H-bonding and π - π stacking interaction linking the molecule of **1** with four neighbouring molecules (O8–H8…O2: green dashed line; O4–H8…O6: pink dashed line; π - π stacking interaction: yellow dashed line); (b) the structural representation of the distorted tetrahedral geometry of the molecule linked with adjacent molecules; (c) the topological structure of the two-fold interpenetrating diamondoid framework of **1**.

sustained through coordination bonds directly.¹³ Careful examination of the crystal structure reveals that molecular cluster **1** exhibits a two-fold interpenetrated framework. The driving force to generate the two-fold interpenetration is conventional N–H···O H-bonding, which is formed between the lattice water molecules and the nitrogen atoms from the ligands (Fig. S4, ESI†).

Crystal structure of 2

The reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with H_3L (4 : 1 molar ratio) in CH₃OH-DMF (2:2 volume ratio) produces yellow crystals of $[Zn_4(HL)_2(CH_3COO)_4]$ ·2(DMF)·2(CH₃OH) (2) in an 82% yield, the molecular structure of which was determined by single-crystal X-ray diffraction, as depicted in Fig. 1b. The molecular cluster 2 crystallizes in a triclinic space group and is linear. Two asymmetrical units [Zn₂(HL)(CH₃COO)₂] in 2 are bridged through the hydroxyl group at the 3-position in the HL²⁻ ligand. In each asymmetrical unit, the HL²⁻ ligand coordinates to two Zn atoms with imine-nitrogen, carbonyl-oxygen and bridging phenoxooxygen atoms combined with two bridging acetate ligands (synsyn mode). The Zn1-Zn2 distance in the asymmetrical unit is 3.2805 Å and that of Zn2-Zn2# between the two asymmetrical units is 3.1576 Å. The coordination mode of the HL^{2-} ligand in 2 displays a $\eta^2:\eta^2:\eta^1:\eta^1:\mu_3$ chelating-bridging mode (Scheme S3b, ESI[†]), which differs from what is observed in 1. The Zn(II) centres are also five coordinated with slightly different coordination environments of Zn1-NO4 and Zn2-O5, respectively. Alternatively, the coordination geometry of Zn(II) in 2 can be regarded as an intermediate between a squared-based pyramid and a trigonal bipyramid (Zn(1): $\tau = 0.48$; Zn(2): $\tau = 0.49$). As expected, the ligand/ acetate binary "blend" strategy in 2 means the molecular structure of 2 differs from that of 1. The acetate anion acts as a bridging ligand in the $[Zn_2(HL)(CH_3COO)_2]$ fragment.¹⁴ Based on the fragmentation info, 2 can be classified as a dimer-of-dimers structure.¹⁵ The linear $Zn_4(HL)_2$ core is almost coplanar (Fig. S5, ESI[†]). The coordinated acetate ligands are located up and down



Fig. 3 (a) UV-vis spectra and (b) normalized emission spectra of the ligand $H_3L,\,\,1$ and 2 in the solid state at room temperature.

the plane. The molecules are linked from a 1D chain through unconventional H-bonding between the acetate anions (Fig. S6, ESI†). Then, the 1D chain is extended to a 2D layer by hydrogen bonding between solvent CH_3OH and the amide nitrogen atom located in the chain (Fig. S7b, ESI†).

Spectroscopic properties of H₃L, 1 and 2

Electronic absorption spectra of H_3L , 1 and 2. In the absorption spectra of molecular clusters 1 and 2 measured on a BaSO₄ plate, three peaks at 233, 309 and ~425 nm for 1, and 240, 313 and ~425 nm for 2, respectively, are observed. The H_3L ligand on an BaSO₄ plate is observed to absorb at 234 and 322 nm. The 233 and 309 nm absorptions for 1 (240 and 313 nm for 2) may be assigned as π - π * charge transfer, similar to the 234 and 322 nm peaks of the free ligand, and the relatively lower peak (~425 nm) is a result of MLCT transition (Fig. 3a).¹⁶

Photoluminescent properties of H₃L, 1 and 2. Zinc complexes with Schiff base ligands are known for their fascinating luminescence properties, with emission bands currently located between 390 and 590 nm.¹⁷ The photoluminescent behaviours of $\mathbf{1}, \mathbf{2}$ and the free ligand $\mathbf{H}_{3}\mathbf{L}$ were studied in the solid state at room temperature (Fig. 3b). Under λ = 309 nm excitation, the emission for molecular cluster 1 is at 556 nm, accompanied by a shoulder peak at 402 nm. Compared to the emission of the free ligand (λ_{em} = 471 and 550 nm, λ_{ex} = 322 nm), the peaks at 402 and 556 nm can be attributed to ligand-to-metal charge transfer (LMCT) and π - π * intraligand (IL) transitions of the ligand. Molecular cluster 2 exhibits green luminescence with a peak maximum centered on $\lambda_{\rm em}$ = 540 nm when $\lambda_{\rm ex}$ = 312 nm. The electronic absorption spectra and photoluminescence properties of the ligand H₃L, 1 and 2 in solution were studied to further understand the solution behaviour (section 6, ESI[†]).

Conclusions

Based on this "key" ligand, two tetranuclear Zn(II) molecular clusters have been synthesized successfully. Molecular cluster **1** is a boat-shaped, closed-cluster and assembled into a diamondoid supramolecular framework through strong hydrogen bonding, which is quite unusual. Molecular cluster **2** is a linear opencluster. The UV-vis and photoluminescent properties of both clusters were characterized in the solid state and ethanol. Within a wide range of wavelengths, the clusters can emit different colours, implying the solvent polarity and H-bonding donor (HBD) has an effect on their fluorescence properties.

Experimental

Materials and instrumentation

All the starting materials and solvents used in this work were commercially available and of analytical grade from Alfa Aesar Chemical Company without further purification. Organic solvents of analytical purity were supplied by commercial sources and were used as received. Elemental analyses (C, H, N) were performed on a Flash EA1112 microanalyzer at the Beijing Institute of Technology. The FT-IR spectrum was recorded in a Nicolet-360 FT-IR spectrometer as KBr pellets in the 4000–400 cm^{-1} region. The UV-vis absorption spectra were examined on a JASCO UV-1901 spectrophotometer in the wavelength range of 200-800 nm. The photoluminescent (PL) spectra were recorded by a Hitachi F-7000 luminescence spectrophotometer equipped with a 450 W xenon lamp as the excitation source. Measurements were collected at room temperature. The photomultiplier tube voltage was 700 V, the scan speed was 1200 nm min⁻¹ and the slit width was 2.5 nm (5.0 nm). Thermogravimetric analyses (TGA) were carried out on a SEIKO TG/DTA 6200 thermal analyzer from room temperature to 800 °C at a ramp rate of 10 °C min⁻¹ in a flowing 150 mL min⁻¹ nitrogen atmosphere. X-ray powder diffraction (XPRD) of the samples were measured using a Rigaku D/max y A X-ray diffractometer equipped with graphite-monochromatized Cu-Ka radiation ($\lambda = 0.154060$ nm). ESI-mass spectra were recorded on a Bruker Apex IV FTMS. ¹HNMR and ¹³C NMR spectra were recorded on a Bruker ARX400 spectrometer (400 and 75 MHz, respectively) instrument in DMSO-d⁶ with Me₄Si as the internal standard.

X-ray crystallographic refinement details

Suitable single crystals with dimensions of $0.16 \times 0.16 \times 0.10$ mm and $0.42 \times 0.18 \times 0.10$ mm for molecular clusters **1** and **2** were selected for single-crystal X-ray diffraction analysis, respectively. Diffraction intensities for the two molecular clusters were collected on a Rigaku RAXIS-RAPID CCD diffractometer equipped with graphite-monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å) using the ω scan mode at 153 K. The diffraction intensity data were collected in the θ range of $3.00-27.47^{\circ}$ for **1** and $2.72-25.02^{\circ}$ for **2**. The collected data were reduced using the SAINT software and empirical absorption corrections were performed using the SADABS software.¹⁸ The two structures were solved by direct methods¹⁹ and refined using full-matrix least square techniques on F^2 (ref. 20) with the program SHELXL-97.¹⁸ All non-hydrogen atomic positions were located in difference Fourier maps and

Table 1 Crystal data of molecular cluster 1 and 2

	1	2
Empirical formula	$C_{65}H_{67}N_{11}O_{22}Zn_4$	$C_{44}H_{54}N_6O_{20}Zn_4$
Formula weigh	1615.86	1248.41
Crystal system	Tetragonal	Triclinic
Space group	$Par{4}$	$P\bar{1}$
a (Å)	14.789(2)	10.508(2)
b (Å)	14.789(2)	10.684(2)
c (Å)	17.044(3)	12.276(3)
α(°)	90	112.10(3)
β()	90	104.75(3)
γÕ	90	90.29(3)
$V(Å^3)$	3727.9(11)	1671.0(6)
Z	2	1
T (K)	153.1500	153.1500
$D_{\rm c} ({\rm mg \ m^{-3}})$	1.439	1.690
$\mu (\mathrm{mm}^{-1})$	1.350	0.981
F(000)	1658	640
$\hat{\theta}_{\min}, \hat{\theta}_{\max}$ (°)	3.00, 27.47	2.72, 25.02
S	1.089	0.981
R _{int}	0.0544	0.0282
Final R_1 , $wR_2 [I > 2\sigma(I)]$	0.0641, 0.1685	0.0263, 0.0630
R_1, wR_2 (all data)	0.0848, 0.182	0.0351, 0.0657
Peak and hole (e $Å^{-3}$)	0.960, -0.489	0.321, -0.314

refined anisotropically. Some of the hydrogen atoms were placed in their geometrically generated positions and other hydrogen atoms were located from the difference Fourier map and refined isotropically. The crystallographic data are given in Table 1. Selected bond distances and angles are given in Table S1, ESI.[†] CCDC 877843 (1) and CCDC 877844 (2) contain the supplementary crystallographic data for this paper.

Synthesis of the H₃L ligand

An ethanol (20 mL) solution of 2,3-dihydroxybenzaldehyde (1.381 g, 0.01 mol) was added dropwise to a stirring ethanol (20 mL) solution of 4-hydroxybenzoylhydrazine (1.522 g, 0.01 mmol). The addition of 1 drop of concentrated hydrochloric acid induced a color change along with immediate precipitation. Then the mixture was refluxed for 8 hours with vigorous stirring and subsequently cooled to room temperature. The gray precipitation was collected by vacuum filtration, washed with ethanol and diethyl ether, and dried in air (Scheme S1, ESI[†]). Yield: (72%). Anal. calcd for C14H12N2O4: C, 61.76; H, 4.41; N, 10.29. Found: C, 61.69; H, 4.38; N, 10.32. Selected IR (KBr pellet, cm⁻¹): v(O–H) 3328 (m); v(C=O) 1654 (s); $v(C=N)^+$ amide 1615, 1587 (m). ¹HNMR (400 MHz, DMSO-*d*⁶): δ (ppm) 8.44 (s, 1H), 7.84 (s, 1H), 7.82 (m, 2H), 6.90 (m, 2H), 6.80 (m, 1H), 6.78 (m, 1H), 6.76 (m, 1H), 6.19 (s, 3H). ¹³CNMR $(75 \text{ MHz}, \text{DMSO-}d^6) \delta (\text{ppm}) 162.50, 160.94, 148.37, 146.06, 145.59,$ 129.76, 123.25, 120.21, 119.12, 118.81, 117.29, 115.17. ESI-MS: m/z (100%) 273.1 $[M + 1]^+$.

Synthesis of the molecular cluster $[Zn_4(HL)_4]$ ·3(DMF)·3(H₂O) (1). A solution of $Zn(ClO_4)_2$ ·6H₂O (38 mg, 0.1 mmol) and H₃L (28 mg, 0.1 mmol) in 12 ml DMF–CH₃OH–H₂O (1 : 3 : 2 volume ratio) was stirred into a methanol solution of NaOH (0.1 mmol) for 15 minutes. The resulting yellow solution was left unperturbed to allow slow evaporation. Yellow single crystals suitable for X-ray diffraction analysis were formed after three days. Yield: 65%. Anal. calcd for C₆₅H₆₇N₁₁O₂₂Zn₄: C, 48.27; H, 4.15; N, 9.53. Found: C, 48.28; H, 4.11; N, 9.57. Selected IR (KBr pellet, cm⁻¹): v(Ar–O) 3186, 3048 (w); v(C=O) 1656 (s); v(C=N)⁺ amide 1607, 1584 (m).

Synthesis of the molecular cluster $[Zn_4(HL)_2(CH_3COO)_4]$. 2(DMF)·2(CH₃OH) (2). Zn(CH₃COO)₂·2H₂O (44 mg, 0.2 mmol) in 4 mL of methanol was added to a 10 mL CH₃OH–DMF mixture (2 : 3 volume ratio) of H₃L (14 mg, 0.05 mmol) with continuous stirring *ca.* 30 minutes. The resultant solution was then filtered and left at room temperature as a transparent yellow solution. Yellow single crystals suitable for X-ray analysis were produced by slow evaporation for one day. Yield: 82%. Anal. calcd for C₄₄H₅₄N₆O₂₀Zn₄: C, 42.33; H, 4.36; N, 6.73. Found: C, 42.28; H, 4.35; N, 6.77. Selected IR (KBr pellet, cm⁻¹): ν (Ar–O) 3304, 3204 (w); ν (C=O) 1658 (s); ν (C=N)⁺ amide 1608, 1588 (m); ν as (CO2) 1548 (m); ν as (CO2) 1383 (m).

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