Synthesis, Crystal Structure and Luminescence Properties of "Paddle Wheel" and "Butterfly" Shaped Polynuclear Complexes

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ABSTRACT

A series of metal cluster-based complexes was constructed from the reaction of metal ions (Fe^{III} , Cu^{II} , Zn^{II}) and ligand (2-((2-[2-carboxybenzoyl]oxy)-ethoxy)carbonyl)benzoic acid) (H_2L) in $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OH , $(\text{C}_2\text{H}_5)_3\text{N}$ and $\text{C}_2\text{H}_5\text{N}$. Two paddle wheel trinuclear clusters $[\text{Fe}_3(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-L})_3(\text{CH}_3\text{OH})_3]\text{NO}_3\cdot\text{C}_2\text{H}_5\text{OH}\cdot\text{CH}_3\text{OH}$ (1) and $[\text{Fe}_3(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-L})_3(\text{H}_2\text{O})_3]\text{NO}_3\cdot 5\text{CH}_3\text{OH}\cdot\text{H}_2\text{O}$ (2), one tetranuclear cluster $[\text{Cu}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_5\text{N})_2\cdot 2\text{C}_2\text{H}_5\text{N}]_2$ (3) and one butterfly shaped dinuclear cluster $[\text{Zn}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_5\text{OH})_2]\cdot 2\text{CH}_3\text{OH}$ (4) were obtained. Complexes 1, 2, and 4 are further assembled by intermolecular hydrogen bonds to form supramolecular frameworks. In complex 3, the flexible benzoic acid ligand chelates with two Cu^{II} , which induces a decrease of Cu–Cu intermetallic separation (rang from 2.644 to 2.657 Å). The structures of the complexes are characterized by IR spectra, thermal gravimetry (TG), single crystal X-ray diffraction analysis, powder X-ray diffraction (PXRD) and HRMS spectra. The luminescent properties of the clusters 1-4 are also studied, the results show that the cluster 4 exhibits blue fluorescence at room temperature.

1. Introduction

Novel coordination polyhedrons have received much attention due to their great potential applications[1], such as catalysis[2], magnetism[3], luminescence[4] and gas storage[5]. One promising approach for the construction of coordination polyhedrons is based on the self-assembly of cluster-based complex composed of polynuclear cluster as secondary building unit (SBU) and bridging organic linkers[6]. Usually, linear dicarboxylic acids as linkers may be used to assembly transition-metal ions into polynuclear clusters through a network of bridges[7]. The modification on

these typical ligands by changing the length, rigidity and flexibility of the spacer moiety give rise to versatile polynuclear clusters, which facilitate nontrivial heterogeneous catalytic[8], sorption/desorption[9], photochemical[10] and magnetic properties[11].

In this work, we attempted the assembly of polynuclear clusters by selecting multifunctional dicarboxylic acid 2-((2-[2-carboxybenzoyl]oxy)-ethoxy)carbonyl) benzoic acid (H_2L) as an organic ligand (Scheme 1, right). The H_2L ligand with flexible $-CH_2-CH_2-$ group and two carboxylic groups in opposite directions can bend and rotate freely when it coordinates with metal centers, which allows for conformation of polynuclear cluster. **Therefore, di-, tri-, and tetranuclear cluster-based complexes were synthesized.** Further, the luminescent properties of the complexes have been investigated. This work aims to provide an optional route for the construction of polynuclear clusters that can be used as a vertex to construct coordination polyhedron.

Scheme 1. The synthesis route of the metal complexes.

2. Experimental

2.1 Materials and methods

All reagents and solvents were purchased commercially and used without further purification. IR spectra were obtained using KBr pellets on a NEXUS-670 FTIR spectrometer from 400 to 4000 cm^{-1} . C, H, and N elemental analyses were performed on a Perkin–Elmer PE-2400 elemental analyzer. Thermal gravimetric analyses were carried out by using a STA 409PC DSC/TGA/DTA thermal analyzer under a simulated air condition (5 ml/min O_2 ; 20 ml/min N_2) from 30 to 800°C at a heating rate of 10°C/min. **HRMS data were obtained on a Bruker QTOF mass spectrometer, equipped with an electrospray ionization (ESI) source. Powder X-ray diffraction (PXRD) measurements on complexes 1 and 2 were performed on a Panalytical X-Pert X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), in which the X-ray tube was operated at 40 kV and 40 mA. Solid-state luminescence spectra were recorded on a FLS 920 spectrofluorometer equipped with a 450W xenon lamp as excitation source.**

Table 1Crystal data and structure refinement for **1-4**

CCDC	857830	857831	857829	857833
Empirical formula	C ₆₀ H ₅₈ Fe ₃ NO ₃₃	C ₅₉ H ₆₆ Fe ₃ NO ₃₇	C ₄₄ H ₃₆ Cu ₂ N ₄ O ₁₆	C ₄₂ H ₄₄ O ₂₀ Zn ₂
Formula weight	1488.62	1548.68	1003.85	999.51
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>P-1</i>
<i>a</i> (Å)	21.828(2)	13.1139(11)	15.9770(16)	8.7550(7)
<i>b</i> (Å)	13.7370(15)	24.161(2)	13.6868(11)	11.7949(11)
<i>c</i> (Å)	44.609(4)	23.382(2)	41.493(3)	11.9551(13)
α (°)	90	90	90	75.896(2)
β (°)	92.3810(10)	91.9920(10)	91.7100(10)	72.2640(10)
γ (°)	90	90	90	72.8520(10)
<i>V</i> (Å ³)	13364(2)	7404.1(11)	9069.4(14)	1107.41(18)
<i>Z</i>	8	4	8	1
<i>T/K</i>	298(2)	298(2)	298(2)	298(2)
Density calculated (Mg/m ³)	1.480	1.480	1.470	1.499
Absorption coefficient (mm ⁻¹)	0.736	0.671	1.013	1.163
<i>F</i> (000)	6136	3204	4112	516
Goodness-of-fit on <i>F</i> ²	1.070	1.046	1.086	1.067
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0724, <i>wR</i> 2 = 0.1855	<i>R</i> 1 = 0.1198, <i>wR</i> 2 = 0.3017	<i>R</i> 1 = 0.1478, <i>wR</i> 2 = 0.3686	<i>R</i> 1 = 0.0356, <i>wR</i> 2 = 0.0774
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1083, <i>wR</i> 2 = 0.2018	<i>R</i> 1 = 0.2522, <i>wR</i> 2 = 0.3551	<i>R</i> 1 = 0.2230, <i>wR</i> 2 = 0.4183	<i>R</i> 1 = 0.0510, <i>wR</i> 2 = 0.0856
Largest diff. peak and hole(e.Å ⁻³)	1.032 and -0.565	0.715 and -0.904	1.450 and -1.836	0.426 and -0.341

2.2 X-ray crystallographic studies

Data were collected at 298(2) by using a Bruker Smart 1000 CCD detector with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). Absorption effects were corrected empirically by using SADABS[12]. The structure was solved by applying direct methods with SHELXS-97 and refined by employing full-matrix least squares based on *F*² with SHELXL-97[13]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located and refined geometrically. The crystal data and the structural refinement parameters are listed in Table 1. The selected bond lengths and bond angles are shown in Table 2.

Table 2

Selected Bond Lengths and Bond Angles

Complex 1		Complex 2		Complex 3		Complex 4	
<i>Bond length (Å)</i>							
Fe1-O25	1.915(4)	Fe1-O25	1.926(7)	Cu1-O7	1.936(12)	Zn1-O9	1.971(2)
Fe1-O18	2.015(4)	Fe1-O20	1.989(10)	Cu1-O3	1.951(12)	Zn1-O3	2.023(2)
Fe1-O1	2.029(4)	Fe1-O3	2.008(8)	Cu2-N2	2.174(17)	Zn1-O7	2.041(2)
Fe1-O3	1.998(4)	Fe1-O7	2.027(9)	Cu1-N1	2.204(16)	Zn1-O8	2.058(2)
Fe1-O26	2.047(4)	Fe1-O24	2.029(9)	Cu1-Cu2	2.644(3)	Zn1-O4	2.031(2)
Fe1-O20	2.019(4)	Fe1-O26	2.052(8)	Cu1-O15	1.988(12)	Zn1-Zn1	2.984(7)
				Cu1-O11	1.984(12)		
				Cu3-Cu4	2.657(3)		
<i>Bond Angle(°)</i>							
O25-Fe1-O18	93.98(16)	O25-Fe1-O3	95.4(3)	O7-Cu1-O3	90.2(5)	O9-Zn1-O3	97.75(9)
O25-Fe1-O20	96.87(15)	O25-Fe1-O7	94.6(3)	O7-Cu1-N1	93.0(6)	O3-Zn1-O4	158.67(9)
Fe2-O25-Fe1	120.28(18)	O3-Fe1-O7	91.1(3)	O3-Cu1-N1	98.5(6)	O9-Zn1-O4	103.58(10)
Fe2-O25-Fe3	119.25(18)	Fe3-O25-Fe1	121.1(3)	O7-Cu1-O11	169.0(5)		
O3-Fe1-O1	91.23(16)	Fe3-O25-Fe2	119.3(3)	O15-Cu1-N1	92.8(6)		
Fe1-O25-Fe3	120.42(18)	Fe1-O25-Fe2	119.5(3)	O12-Cu2-N2	95.1(6)		
				O8-Cu2-O4	89.0(5)		
				O12-Cu2-O16	90.0(5)		

2.3 Syntheses of complexes

2.3.1 Synthesis of $[Fe_3(\mu_3-O)(\mu_2-\eta^2-L)_3(CH_3OH)_3]NO_3 \cdot C_2H_5OH \cdot CH_3OH$ (1)

H₂L (0.0716 g, 0.2 mmol) and Fe(NO₃)₃·9H₂O (0.0405 g, 0.2 mmol) were added to a mixture of ethanol (5 ml), methanol (10 ml) and triethylamine (2 ml) with a molar ratio of 0.25:0.86:1. The mixture was stirred for 1 h at room temperature and filtered. The filtrate slowly evaporated for 5 days to obtain orange rectangular crystals for X-ray analysis. Elemental analysis calcd (%) for C₆₀H₅₈Fe₃NO₃₃: C, 48.37; H, 3.89; N, 0.94; found(%): C, 46.84; H, 3.85; N, 0.83.

2.3.2 Synthesis of $[Fe_3(\mu_3-O)(\mu_2-\eta^2-L)_3(H_2O)_3]NO_3 \cdot 5CH_3OH \cdot H_2O$ (2)

H₂L (0.0716 g, 0.2 mmol) and Fe(NO₃)₃·9H₂O (0.0405 g, 0.2 mmol) were added to a mixture of methanol (5 ml) and water (10 ml). The experiment was performed using the procedures described in **1**. Orange rectangular crystals were obtained. Elemental analysis calcd (%) for C₅₉H₆₆Fe₃NO₃₇: C, 45.72; H, 4.26; N, 0.90; found (%): C, 44.17; H, 4.10; N, 1.12.

2.3.3 Synthesis of $[Cu_2(\mu_2-L)_2(C_2H_3N)_2 \cdot 2C_2H_3N]_2$ (3)

H₂L (0.0716 g, 0.2 mmol) and Cu(NO₃)₂·3H₂O (0.0485 g, 0.2 mmol) were added to a mixture of ethanol (5 ml), methanol (10 ml) and triethylamine (2 ml) with a molar ratio of 0.25:0.86:1. After the mixture was stirred for 1 h at room temperature and filtered, the blue solids were obtained. The products were separated and recrystallized in acetonitrile. Suitable blue rectangular crystals were obtained from the blue acetonitrile solution upon evaporation at room temperature for 24 h. Elemental analysis calcd (%) for C₄₄H₃₆Cu₂N₄O₁₆: C, 52.637; H, 3.586; N, 5.581; found (%): C, 50.88; H, 3.711; N, 4.65.

2.3.4 Synthesis of $[Zn_2(\mu_2-L)_2(C_2H_5OH)_2] \cdot 2CH_3OH$ (4)

H₂L (0.0716 g, 0.2 mmol) and Zn(NO₃)₂·6H₂O (0.0485 g, 0.2 mmol) were added to the mixture of ethanol (5 ml), methanol (10 ml), and triethylamine (2 ml) with a molar ratio of 0.25:0.86:1. After the mixture was stirred for 1 h at room temperature, a colorless transparent solution was produced. The solution slowly evaporated for 5 days. Colorless rectangular crystals suitable for X-ray analysis were then obtained. Elemental analysis calcd (%) for C₄₂H₄₄O₂₀Zn₂: C, 50.425; H, 4.40; N, 0; found (%): C, 48.975; H, 4.38; N, 0.025.

3. Results and discussion

3.1 Syntheses and Infrared analysis

Following the synthetic routes shown in Scheme 1, di-, tri-, and tetranuclear complexes **1–4** were synthesized. Complex **1** was prepared as follow: Iron(II) nitrate and H₂L ligand were added to a mixture of ethanol, methanol, and triethylamine. The mixture was allowed to undergo constant stirring for 1h under room temperature. The obtained solution was filtered and then allowed to crystallize by slow evaporation in the air over 5 days to gave the trinuclear complex [Fe₃(μ₃-O)(μ₂-η²-L)₃(CH₃OH)₃]NO₃·C₂H₅OH·CH₃OH (**1**). In contrast, using the same starting materials, but the addition of ethanol and triethylamine was replaced with water, afforded the water coordinated trinuclear complex [Fe₃(μ₃-O)(μ₂-η²-L)₃(H₂O)₃]NO₃·5CH₃OH·H₂O (**2**). Actually, accompany with the formation of a major amount of Fe(III) trinuclear complex, a tiny amount of byproducts was also observed. The experimental PXRD patterns for complex **1**, **2** and the single crystal simulated patterns are depicted in Fig. S1, S2 of the Supplementary Information (SI). The peak positions of the experimental patterns for the complexes nearly matched with the simulated patterns generated from single-crystal X-ray diffraction data, but a small double peak appeared in Fig. S2, indicating the byproducts were formed in complex **2**. The same procedures were used for the preparation of tetranuclear complex [Cu₂(μ₂-L)₂(C₂H₃N)₂·2C₂H₃N]₂ (**3**) and dinuclear complex [Zn₂(μ₂-L)₂(C₂H₅OH)₂]·2CH₃OH (**4**) except copper(II) and zinc(II) nitrate in place of iron(III) nitrate in **1**, respectively, and the resultant precipitate of **3** was separated and

recrystallized in acetonitrile solution. The yields for **1–4** range from ca. 20 to 30%. Yields of the obtained pure fractions are based on starting materials.

The IR spectra of **1–4** (Fig. 1) show strong peaks at 1724 cm^{-1} because of the presence of ester groups in the L ligands. The characteristic bands of carboxylate groups occur at 1610 , 1605 , 1631 and 1639 cm^{-1} for the asymmetric stretching and at approximately 1407 cm^{-1} for symmetric stretching. $\Delta\nu$ (vas – vs) $< 200\text{ cm}^{-1}$, which indicates the presence of bidentate motifs[14] in **1–4**. The weak peaks in the region of $751\text{--}655\text{ cm}^{-1}$ are assigned to the characteristic bands of benzene ring.

Fig. 1. IR spectra of the complexes **1–4**.

3.2 Description of the structure

Single-crystal X-ray diffraction studies revealed that complex **1** is a discrete trinuclear cluster containing a Fe_3O core. As shown in Fig. 2a, Fe1 center is coordinated with six oxygen atoms: four from carboxylate oxygen atoms (O1, O3, O18, and O20) of two different L ligands, one from coordinated methanol (O26) and one from μ_3 -O25, thus the coordination geometry of Fe1 can be described as a distorted octahedral stereochemistry. Similar coordination geometry was also observed for Fe2 and Fe3 in the structure. In **1**, each flexible L ligand bends to form Ω shape and coordinates with adjacent Fe ions via its terminal carboxylate oxygen atoms. The macrocyclic chelate rings cause the complex to possess paddle wheel Fe_3 cage conformation (Fig. 2b). The mean Fe1–O (carboxylate), Fe1–O26, and Fe1–O25 bond lengths are 2.015, 2.047 and 1.915 Å, respectively. These findings are consistent with $[\text{Fe}_3\text{O}]$ triangular cluster observed in a previous work [15]. Moreover, one ethanol molecule, one methanol molecule and one nitrate ion (as a balance charge) appear in the lattice.

Fig. 2 View of the molecular structure of **1**: (a) The coordination environment and (b) the paddlewheel configuration and distorted octahedron geometry (H atoms are omitted for clarity).

When ethanol solvent was replaced with water during the synthesis of **1**, another similar complex **2** was formed (Fig. 3). The structure of **2** also exhibits distorted octahedron geometry and displays the same Fe coordination environment as **1** except three H₂O molecules are coordinated with three Fe centers instead of three methanol molecules. Five methanol molecules, one lattice water molecule and one **nitrate ion** exist in the **lattice**.

Fig. 3 View of the coordination environment of Fe atoms in **2** (H atoms are omitted for clarity).

Both complexes **1** and **2** form supramolecules because of the presence of enrich intermolecular hydrogen bonds. In **1**, each NO₃⁻ group forms intermolecular hydrogen bonds via O29, O30 and O31 with one coordinated methanol (O27) and one lattice methanol molecule (O33), the O27...O29, O27...O30, and O33...O31 distances are 3.206, 2.751, and 2.775 Å, respectively; the corresponding angles of O27-H27...O29, O27-H27...O30, and O33-H33...O31 are 142.78°, 160.48°, and 151.40°.

respectively. At the same time, complex **1** also exhibits intermolecular hydrogen bonds among one lattice methanol (O33), two coordinated methanol (O26, O28) one lattice ethanol (O32) and the middle ester carbonyl oxygen O22 of the adjacent L ligand. Thus, the discrete complex **1** further extends by hydrogen bonded interactions to form a one-dimensional Z shape-chains supramolecule. (Fig. S3 of the SI). Similar to complex **1**, the NO_3^- groups display intermolecular hydrogen bonds via O34 and O36 with the lattice methanol molecules (O29, O32) and the lattice water molecule (O37) ($\text{O29}\cdots\text{O34} = 3.011\text{\AA}$; $\text{O32}\cdots\text{O36} = 2.911\text{\AA}$; $\text{O37}\cdots\text{O34} = 2.861\text{\AA}$). Hydrogen bonds are also exist among the lattice water molecule (O37), coordinated water molecules (O26, O27, O28), lattice methanol molecules (O29, O30, O31, O32), uncoordinated carboxylate oxygen atoms (O2, O6, O10) and the middle ester carbonyl oxygen O22 of the adjacent L ligands. Unlike complex **1**, the packing diagram of **2** exhibits a two-dimensional hydrogen bonding network (Fig. S4 of the SI). The formations of the trinuclear structures of **1** and **2** were confirmed by HRMS data (Fig. S8, S9 of the SI).

Four crystallographically independent Cu^{II} ions with the same coordination environment exist in **3**, where two centrosymmetric $\text{Cu}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_3\text{N})_2$ units construct a tetranuclear cluster. In each $\text{Cu}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_3\text{N})_2$ unit, Cu^{II} is coordinated with five atoms: four oxygen atoms from different L ligands and one nitrogen atom from acetonitrile (Fig. 4). As a result, the coordination environment for Cu^{II} can be described as square pyramidal geometry (Fig. S5 of the SI). The average bond distances of Cu–O (carboxylate) and Cu–N are 1.965 and 2.215 Å, respectively. These values are within normal ranges. Similar to $[\text{Cu}(\text{L}1)\cdot\text{EtOH}]_2$ complex[16], the aromatic dicarboxylate groups act as a tetradentate ligand that bridges two neighboring Cu^{II} ions in a bidentate mode. This coordination mode possibly lead to the Cu–Cu distances (Cu1–Cu2, 2.644 Å; Cu3–Cu4, 2.657 Å) are slightly shorter compared to distance found in other bridged dimers $\text{Cu}\cdots\text{Cu}$ separation [17].

Fig. 4. View of the coordination environment of Cu atoms in **3** (H atoms are omitted for clarity).

In **4**, the dinuclear cluster is composed of two Zn^{II} ions, two L ligands and two ethanol molecules (Fig. 5). Each Zn1 center is five coordinated by oxygen atoms: four carboxylate oxygen atoms (O3, O4, O7, and O8) from two different L ligands and one from the coordinated ethanol molecule (O9). Thus, a distorted square pyramidal geometry is constructed. Two adjacent Zn^{II} ions of the dinuclear cluster are 2.984 Å apart. Each L ligand is chelated to two Zn^{II} ions via two carboxylate groups by bridging bidentate mode and thus constructs a butterfly-like plane. There are intermolecular hydrogen bonds between the lattice methanol molecules (O10) and the adjacent coordinated ethanol (O9), the carboxylate oxygen O4 of the L ligand, respectively. Thus, the intermolecular hydrogen bonds link the

adjacent discrete complex **4** into a one-dimensional chain along the *a* - axis direction. (Fig. S6 of the SI)

Fig. 5. View of the coordination environment of Zn atoms in **4**
(H atoms are omitted for clarity).

3.3 Thermogravimetric (TG) analyses

The TG results of complexes **1-4** are shown in Fig. S7 of the SI. For **1** (Fig. S7(a)), 77.24% weight loss occurred from 30 to 456°C because of the removal of three coordinated methanol molecules and three organic L ligands (calculated: 78.03%). We found that one uncoordinated ethanol molecule and one methanol molecule volatilized from the structure before the signal was checked at 30°C. This finding is consistent with elemental analysis results. Likewise, one free ethanol molecule and one free methanol molecule volatilized from **2** before TG detection was performed (Fig. S7(b)). The weight loss of 81.18% from 30 to 415°C was attributed to the removal of three organic L ligands and three coordinated water molecules (calculated: 82.97%). For **3**, only one acetonitrile was removed from the frameworks before the signal was checked at 30°C. After that 73.76% weight loss was detected from 30 to 314°C, and this phenomenon is accounted for the removal of decomposed organic L ligands (calculated: 73.96%; Fig. S7(c)). The elemental analysis results of **2** and **3** also confirmed the TG results. The weight of **4** was continuously lost from 30 to 800°C. No clear plateau of weight loss was recorded in the entire process. The results reveal that **4** is stable at high temperature up to 614°C, and 81.50% weight loss is attributed to the removal of organic L ligands (calculated: 81.34%; Fig. S7(d)). The decomposition temperature exhibits the following trend: **4** > **1** > **2** > **3**. It indicated that the formation of intermolecular hydrogen bonds in **1**, **2**, and **4** yielded higher thermal stabilities than that of **3**.

3.4 Luminescence properties

The Luminescence properties of complexes **1-4** were studied. The emission spectra of the pure solid powder **4** and the L ligand was obtained at room temperature ($\lambda_{\text{ex}} = 322 \text{ nm}$). The complex **4** exhibited

the maximum fluorescence emission wavelengths at 467 nm among the four complexes (Fig. 6). A similar emission was also observed for the free H₂L ligand with higher intensity. The decrease in the luminescence intensity in **4** was attributed to the fluorescence quenching caused by methanol molecules. The complexes **1-3** did not exhibit any fluorescence, indicating almost complete quenching of fluorescence took place through ligand-to-metal cations (Fe^{III} and Cu^{II}) energy transfer process [18].

Fig. 6. Solid state emission spectra of **4** and the L ligand at room temperature ($\lambda_{\text{ex}} = 322 \text{ nm}$)

4. Conclusion

We successfully synthesized two paddle wheel trinuclear $[\text{Fe}_3(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-L})_3(\text{CH}_3\text{OH})_3]^+$, $[\text{Fe}_3(\mu_3\text{-O})(\mu_2\text{-}\eta^2\text{-L})_3(\text{H}_2\text{O})_3]^+$ cations, one tetranuclear $[\text{Cu}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_3\text{N})_2 \cdot 2\text{C}_2\text{H}_3\text{N}]_2$ clusters and one butterfly-like dinuclear $[\text{Zn}_2(\mu_2\text{-L})_2(\text{C}_2\text{H}_5\text{OH})_2] \cdot 2\text{CH}_3\text{OH}$ cluster by selecting a diester-dicarboxylic ligand containing flexible $(\text{CH}_2)_2$ spacer segment. Reaction conditions, including solvents and starting materials, may be modified to develop various metal cluster-based complexes. We found that the supramolecular structures of **1**, **2** and **4** were constructed through hydrogen bonding interactions between carboxylated groups of the L ligand and the coordinated solvents, uncoordinated solvents and NO_3^- anions. The flexible symmetry dicarboxylate linker plays a significant role in forming short intermetallic distances between $\text{Cu} \cdots \text{Cu}$ in **3**. The four complexes exhibit different thermal stabilities. The thermal stabilities of **1**, **2**, and **4** are higher than that of **3** because hydrogen bonding strengthens their structures. Complex **4** exhibits blue photoluminescence at 467nm^{-1} at room temperature. The possible presence of magnetic property of trinuclear iron cluster is being investigated.

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References

- [1] Y. Ghandour, A. ben Khelifa, M. S. Belkhiria, C. Daiguebonne, S. Freslon, O. Guillou, T. Roisnel, **Crystal structure, physico-chemical and catalytic properties of two organic–inorganic hybrid polyoxometallate-based lanthanide complexes**, *Polyhedron*. 115 (2016) 1-8.
- [2] L. H. Wee, N. Janssens, S. P. Sree, C. Wiktor, E. Gobechiya, R. A. Fischer, J. A. Martens, **Local transformation of ZIF-8 powders and coatings into ZnO nanorods for photocatalytic application**, *Nanoscale*. 6 (2014) 2056-2060.
- [3] X. M. Zhang, J. Lv, F. Ji, H. S. Wu, H. Jiao, P. V. R. Schleyer, **A Perfectly Square-Planar Tetracoordinated Oxygen in a Tetracopper Cluster-Based Coordination Polymer**, *J. Am. Chem. Soc.* 133 (2011) 4788-4790.
- [4] Y. Kang, F. Wang, J. Zhang, X. Bu, **Luminescent MTN-Type Cluster – Organic Framework with 2.6 nm Cages**, *J. Am. Chem. Soc.* 134 (2012) 17881-17884.
- [5] X. L. Yan, S. N. Li, Y. C. Jiang, M. C. Hu, **Synthesis, crystal structures and gas adsorption of two porous pillar-layered MOFs decorated with different functional groups**, *Inorg. Chem. Commun.* 62 (2015) 107-110.
- [6] G. L. Liu, Z. F. Ju, D. Q. Yuan, M. C. Hong, **In Situ Construction of a Coordination Zirconocene Tetrahedron**, *Inorg. Chem.* 52 (2013) 13815-13817.
- [7] P. Mosae. Selvakumar, E. Suresh, P. S. Subramanian, **Hydrogen bonded helices: Synthesis, crystal structure and self-assembled microtubes**, *J. Mol. Struct.* 919 (2009) 72-78.
- [8] R. R. Kuruppathparambil, T. Jose, R. Babu, G. Y. Hwang, A. C. Kathalikkattil, D. W. Kim, D. W. Park, **A room temperature synthesizable and environmental friendly heterogeneous ZIF-67 catalyst for the solvent less and co-catalyst free synthesis of cyclic carbonates**, *Appl. Catal., B: Environmental*. 182 (2016) 562-569.
- [9] B. Mu, F. Li, K. S. Walton, **A novel metal – organic coordination polymer for selective adsorption of CO₂ over CH₄**, *Chem. Commun.* 18 (2009) 2493-2495.
- [10] G. M. Dulcevscaia, I. G. Filippova, M. Speldrich, J. van. Leusen, V. C. Kravtsov, S. G. Baca, P. S. S. Decurtins, **Cluster-Based Networks: 1D and 2D Coordination Polymers Based on {MnFe₂(μ₃-O)}-Type Clusters**, *Inorg. Chem.* 51 (2012) 5110-5117.
- [11] J. K. Schnobrich, O. Lebel, K. A. Cychosz, A. Dailly, A. G. Wong-Foy, J. M. Adam, **Linker-Directed Vertex Desymmetrization for the Production of Coordination Polymers with High Porosity**, *J. Am. Chem. Soc.* 132 (2010) 13941-13948.
- [12] G. M. Sheldrick, **SADABA, Program for Empirical Absorption Correction of Area Detector Data**; University of Gottingen: 1996.
- [13] G. M. Sheldrick, **SHELXL-97**, University of Gottingen, Germany, 1997.
- [14] K. Nakamoto, **Infrared and Raman Spectra of Inorganic and Coordination Compounds, THIRD EDITION**, A Wiley-Interscience Publication.
- [15] E. C. Sañudo, J. S. Uber, A. Pons. A. Balagué, O. Roubeau, G. Aromí, **Molecular [(Fe₃) – (Fe₃)] and [(Fe₄) – (Fe₄)] Coordination Cluster Pairs as Single or Composite Arrays**, *Inorg. Chem.* 51 (2012) 8441-8446.

- [16] P. M. Selvakumar, E. Suresh, P. S. Subramanian, **New macrocyclic Cu(II)-bischelates with paddle wheel Cu₂-acetate cage**, *Inorg. Chim. Acta.* 361 (2008) 1503-1509.
- [17] P. Adak, C. Das, B. Ghosha, S. Mondal, et al., Two pseudohalide-bridged Cu(II) complexes bearing the anthracene moiety: Synthesis, crystal structures and catecholase-like activity, *Polyhedron*. 119 (2016) 39-48.
- [18] G. De Santis, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Taglietti, **Molecular Recognition of Carboxylate Ions Based on the Metal – Ligand Interaction and Signaled through Fluorescence Quenching**, *Angew. Chem. Int. Ed.* 35 (1996) 202-204.