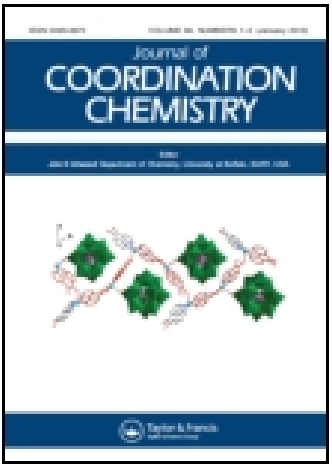
This article was downloaded by: [Institute Of Atmospheric Physics]
On: 09 December 2014, At: 15:41
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Click for updates

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Three polynuclear complexes with bridging triazole ligand: crystal structures

Lei Shen[a], Qiu-Jie Xia[a], Lei Wang[b], Jie Yang[a], Yong Chen[a], Xiao-Yan Tang[a], Yun-Sheng Ma[a], Rong-Xin Yuan[a] & Dun-Ru Zhu[b]

[a] Jiangsu Key Laboratory of Advanced Functional Materials, Department of Chemistry & Materials Engineering, Changshu Institute of Technology, Changshu, PR China

[b] State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, PR China

Accepted author version posted online: 28 May 2014.Published online: 20 Jun 2014.

To cite this article: Lei Shen, Qiu-Jie Xia, Lei Wang, Jie Yang, Yong Chen, Xiao-Yan Tang, Yun-Sheng Ma, Rong-Xin Yuan & Dun-Ru Zhu (2014) Three polynuclear complexes with bridging triazole ligand: crystal structures, Journal of Coordination Chemistry, 67:9, 1573-1583, DOI: 10.1080/00958972.2014.927060

To link to this article: http://dx.doi.org/10.1080/00958972.2014.927060

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing,

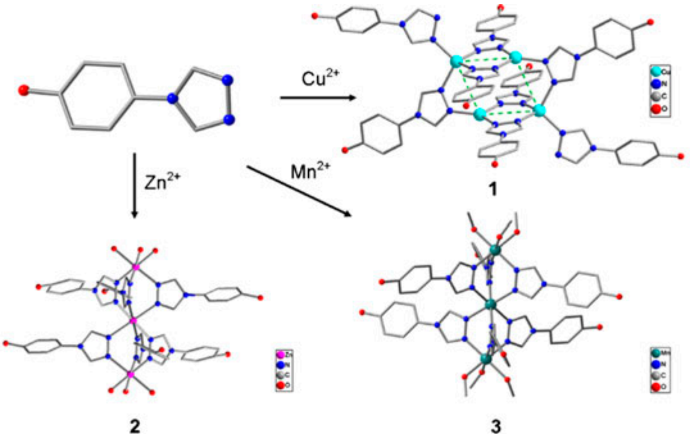
Journal of Coordination Chemistry, 2014
Vol. 67, No. 9, 1573–1583, http://dx.doi.org/10.1080/00958972.2014.927060

Three polynuclear complexes with bridging triazole ligand: crystal structures

LEI SHEN†, QIU-JIE XIA†, LEI WANG‡, JIE YANG†, YONG CHEN†,
XIAO-YAN TANG†, YUN-SHENG MA†, RONG-XIN YUAN*† and DUN-RU ZHU*‡

†Jiangsu Key Laboratory of Advanced Functional Materials, Department of Chemistry & Materials Engineering, Changshu Institute of Technology, Changshu, PR China
‡State Key Laboratory of Materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing, PR China

(*Received 12 June 2012; accepted 25 March 2014*)



Three new complexes with 4-(4-hydroxyphenyl)-1,2,4-triazole (L), $[Cu_4L_8](ClO_4)_4·4H_2O$ (**1**), $[Zn_3L_6(H_2O)_6](ClO_4)_6·6H_2O$ (**2**) and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6·4.5H_2O$ (**3**), have been synthesized and characterized by single crystal X-ray crystallography.

Three polynuclear clusters, $[Cu_4L_8](ClO_4)_4·4H_2O$ (**1**), $[Zn_3L_6(H_2O)_6](ClO_4)_6·6H_2O$ (**2**), and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6·4.5H_2O$ (**3**) (L = 4-(4-hydroxyphenyl)-1,2,4-triazole), obtained by the reactions of $M(ClO_4)_2·6H_2O$ with L have been isolated and structurally characterized. Complex **1** featured a tetranuclear Cu(I) structure. Both **2** and **3** are linear hexapositive trimers linked by three N1,N2–1,2,4-triazole ligands to the divalent central and terminal metal ions. Furthermore, the luminescence properties of **2** were investigated at room temperature in the solid state.

Keywords: Cluster; Polynuclear complex; Luminescence; Copper(I); Zinc(II); Manganese(II)

---

*Corresponding authors. Email: yuanrx@cslg.edu.cn (R.-X. Yuan); zhudr@njtech.edu.cn (D.-R. Zhu)

1. Introduction

1,2,4-Triazole and its derivatives are widely used as ligands in coordination chemistry. As multidentate ligands, the 1,2,4-triazole derivatives are particularly attractive due to different coordination modes and bidentate- or monodentate bridging that depends on the position and the nature of the substituent at the triazole ring, respectively [1]. The 1,2,4-triazole can coordinate to metal ions via the so-called N1,N2-bridging coordination with N1 and N2 positions unsubstituted. The mode leads to polynuclear complexes that often demonstrate magnetic exchange interactions [2–4]. Recently, we have synthesized some mononuclear and dinuclear complexes with substituted 1,2,4-triazole ligands [5]. However, the coordination chemistry of hydroxy-substituted 1,2,4-triazoles has been less investigated. In 2007, two Cu(II) complexes with 4-(4-hydroxyphenyl)-1,2,4-triazole (L) were reported by Lavrenova [6]. In 2011, we reported two linear trinuclear Co(II) and Ni(II) complexes with L [7]. As a continuation of our investigation on complexes with L, the present contribution deals with the synthesis and X-ray structures of three polynuclear clusters, $[Cu_4L_8](ClO_4)_4\cdot4H_2O$ (**1**), $[Zn_3L_6(H_2O)_6](ClO_4)_6\cdot6H_2O$ (**2**), and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6\cdot4.5H_2O$ (**3**).

2. Experimental

2.1. *Materials and methods*

Solvents were dried over activated molecular sieves before use and refluxed over the appropriate drying agents under argon. Other chemicals and reagents were obtained from commercial sources and used as received. Elemental analyses for C, H, and N were performed with an EA1110-CHNS elemental analyzer. The FT-IR spectra were recorded on a Nicolet 380 spectrometer, using pressed KBr pellets. L was synthesized according to the literature method [8].

Determinations of the unit cell and data collection of **1** and **2** were performed on a Rigaku SCX mini CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) at 291 K, while the unit cell parameters and intensity data of **3** were collected at 173(2) K on a Bruker SMART CCD diffractometer. The intensity data were collected by the ω scan technique and were reduced using Crystal Clear [9] or SAINT. The structures were solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 [10]. All non-hydrogen atoms were refined anisotropically and hydrogens were included in the final stage of the refinement on calculated positions, bonded to their carrier atoms. All hydrogens were placed in geometrically idealized positions (C–H = 0.95 Å for phenyl groups) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2\ U_{eq}(C)$, for phenyl groups. In **1**, C27–C32 and O4 of the 4-hydroxyphenyl group on N12 are highly disordered over two sites and refined with an occupancy of 0.709(19) Å for C27A–C32A and O4A, and 0.291(19) Å for C27B–C32B and O4B. O5–O8 and Cl1 of one perchlorate are highly disordered over two sites and refined with an occupancy of 0.422(16) Å for O5A–O8A and Cl1A, and 0.578(16) Å for O5B–O8B and Cl1B. O9–O12 and Cl2 of another perchlorate are also disordered over two sites and refined with an occupancy of 0.747(10) Å for O9A–O12A and Cl2A, and 0.253(10) Å for O9B–O12B and Cl2B. In **2**, C3–C8 and O1 of the 4-hydroxyphenyl group on N3 are highly disordered over two sites and refined with an occupancy of 0.564(8) Å for C3A–C8A and O1A, and 0.436(8) Å for C3B–C8B and O1B. O2–O5 and Cl1 of perchlorate are disordered over two sites and

Table 1. Crystallographic data for **1**–**3**.

Complexes	**1**	**2**	**3**
Molecular formula	$C_{64}H_{64}Cl_4Cu_4N_{24}O_{28}$	$C_{48}H_{66}Cl_6N_{18}O_{42}Zn_3$	$C_{54}H_{75}Cl_6Mn_3N_{18}O_{40.5}$
Formula weight	2013.35	1976.00	2001.80
Size (mm^3)	0.26 × 0.20 × 0.10	0.15 × 0.13 × 0.12	0.25 × 0.23 × 0.22
Crystal color	Green	Colorless	Colorless
Crystal system	Triclinic	Rhombohedral	Cubic
Space group	*P-1*	*R-3*	*Ia*-3
a (Å)	10.565(2)	12.8321(15)	25.632(3)
b (Å)	13.603(3)	12.8321(15)	25.632(3)
c (Å)	15.058(3)	12.8321(15)	25.632(3)
α (°)	92.95(3)	79.805(17)	90
β (°)	93.67(3)	79.805(17)	90
γ (°)	111.30(3)	79.805(17)	90
V (Å^3)	2005.6(7)	2023.5(4)	16,841(3)
Z	1	1	4
D_{Calcd} (g cm^{-3})	1.667	1.622	1.579
T/(K)	291(2)	291(2)	173(2)
μ (mm^{-1})	1.276	1.184	0.735
θ Range (°)	3.05–25.00	3.26–27.47	3.37–25.01
Total reflections	17,045	21,195	25,524
Unique reflections	7053 (R_{int} = 0.1125)	3098 (R_{int} = 0.1059)	2425 (R_{int} = 0.0847)
Parameters	703	263	196
R^{a}	0.0895	0.0609	0.0992
wR^{b}	0.1556	0.1343	0.2284
GOF^{c}	1.049	1.021	1.276
Largest diff. peak and hole (e Å^{-3})	0.835 and −0.596	0.487 and −0.438	1.007 and −0.527

$^{a}R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$.
$^{b}wR = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.
$^{c}\mathrm{GOF} = \{\Sigma w((F_o^2 - F_c^2)^2)/(n\text{-}p)\}^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

refined with an occupancy of 0.51(3) Å for O2A–O5A and Cl1A, and 0.49(3) Å for O2B–O5B and Cl1B. Crystallographic data are listed in table 1. The selected bond lengths and angles are given in table 2.

2.2. *Syntheses of 1–3*

2.2.1. Synthesis of $[Cu_4L_8](ClO_4)4\cdot 4H_2O$ (1). A mixture of $Cu(ClO_4)_2\cdot 6H_2O$ (37.0 mg, 0.1 mM) and 4-(4-hydroxyphenyl)-1,2,4-triazole (32.0 mg, 0.2 mM) in MeOH (10 mL) was sealed in a 25 mL Telfon-lined stainless steel container and heated at 120 °C for 72 h. After the sample was cooled to room temperature at 5 °C/h, the green block crystals were obtained in ca. 67% yield based on Cu. Anal. Calcd for $C_{64}H_{64}Cl_4Cu_4N_{24}O_{28}$ (%): C, 38.18; H, 3.20; N, 16.70. Found: C, 38.36; H, 3.01; N, 16.83. FT-IR (KBr, cm^{-1}): 3435 (br), 1615 (m), 1550 (vs), 1511 (vs), 1112 (s), 1081 (s), 628 (s).

2.2.2. Synthesis of $[Zn_3L_6(H_2O)_6](ClO_4)_6\cdot 6H_2O$ (2) and $[Mn_3L_6(CH_3OH)_6](ClO_4)$ $6\cdot 4.5H_2O$ (3). **2** and **3** were prepared by a similar experimental procedure to **1** except that $Zn(ClO_4)_2\cdot 6H_2O$ and $Mn(ClO_4)_2\cdot 6H_2O$ were used. The colorless crystals of **2** were obtained in ca. 60% yield based on Zn. Anal. Calcd for $C_{48}H_{66}Cl_6N_{18}O_{42}Zn_3$ (%): C, 29.17; H, 3.37; N, 12.76. Found: C, 29.03; H, 3.15; N, 12.54. FT-IR (KBr, cm^{-1}): 3432 (br), 1609 (m), 1551 (vs), 1512 (vs), 1113 (s), 1078 (s), 624 (s). Colorless crystals of **3** were obtained in ca. 50% yield based on Mn. Anal. Calcd for $C_{54}H_{75}Cl_6Mn_3N_{18}O_{40.5}$ (%):

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**3**.

Complex **1**			
Cu(1)–N(4)	1.955(6)	Cu(1)–N(7)	1.957(6)
Cu(1)–N(1)	2.039(6)	Cu(2)–N(5)	2.004(6)
Cu(2)–N(11)	2.030(7)	Cu(2)–N(2)	2.039(6)
Cu(2)–N(8)^A	2.048(6)	Cu(1)···Cu(2)	3.625(5)
Cu(1)···Cu(2)^A	3.575(5)		
N(4)–Cu(1)–N(7)	138.9(3)	N(4)–Cu(1)–N(1)	114.0(3)
N(7)–Cu(1)–N(1)	107.1(2)	N(5)–Cu(2)–N(11)	113.9(3)
N(5)–Cu(2)–N(2)	109.9(3)	N(11)–Cu(2)–N(2)	105.7(3)
N(5)–Cu(2)–N(8)^A	113.7(3)	N(11)–Cu(2)–N(8)^A	108.6(3)
N(2)–Cu(2)–N(8)^A	104.3(3)	C(10)–N(4)–Cu(1)	129.0(5)
N(5)–N(4)–Cu(1)	123.0(5)		
Complex **2**			
Zn(1)–N(1)	2.180(3)	Zn(2)–O(1 W)	2.120(3)
Zn(2)–N(2)	2.119(3)	Zn1···Zn2	3.853(5)
N(1)^A–Zn(1)–N(1)	90.75(12)	N(1)–Zn(1)–N(1)^B	89.25(12)
O(1 W)^B–Zn(2)–N(2)	91.56(15)	O(1 W)^C–Zn(2)–O(1 W)	88.66(14)
O(1 W)–Zn(2)–N(2)^B	88.63(15)	O(1 W)–Zn(2)–N(2)	177.28(15)
Complex **3**			
Mn(1)–N(1)	2.053(5)	Mn(2)–N(2)	2.102(5)
Mn(1)–O(2)	2.076(5)	Mn1···Mn2	3.795(5)
N(1)–Mn(1)–N(1)^A	90.8(2)	N(1)–Mn(1)–O(2)^A	89.8(2)
N(1)^B–Mn(1)–O(2)^B	89.95(19)	N(1)^A–Mn(1)–O(2)	179.1(2)
O(2)–Mn(1)–O(2)^B	89.46(19)	N(2)^A–Mn(2)–N(2)	88.84(19)
N(2)–Mn(2)–N(2)^C	91.16(19)		

Note: Symmetry codes for **1**: A: $1-x, -y, 1-z$. **2**: A: $-y, 1-z, 1-x$; B: $z-1, x, y+1$; C: $y, z-1, x+1$. **3**: A: $y+1/2, 1/2-z, 1-x$; B: $1-z, x-1/2, 1/2-y$; C: $z+1/2, 1-x, y$.

C, 32.40; H, 3.78; N, 12.59. Found: C, 32.14; H, 3.52; N, 12.27. FT-IR (KBr, cm^{-1}): 3434 (br), 1611 (m), 1549 (vs), 1514 (vs), 1116 (s), 1080 (s), 628 (s).

3. Results and discussion

3.1. *Syntheses and spectroscopic properties of 1–3*

The reactions of $M(ClO_4)_2 \cdot 6H_2O$ (M = Cu, Zn, Mn) with L at 120 °C yielded $[Cu_4L_8](ClO_4)_4 \cdot 4H_2O$ (**1**), $[Zn_3L_6(H_2O)_6](ClO_4)_6 \cdot 6H_2O$ (**2**), and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6 \cdot 4.5H_2O$ (**3**), respectively. By varying the reaction parameters such as ligand-to-metal ratio, cooling speed, and the solvent system have not succeeded in the formation of products suitable for single crystal X-ray diffraction analysis for all complexes. The use of $MSO_4 \cdot 7H_2O$ or $M(NO_3)_2 \cdot 6H_2O$ instead of $M(ClO_4)_2 \cdot 6H_2O$ (M = Cu, Zn, Mn) yielded a set of uncharacterized precipitates though identical reaction conditions. The product structure depends on the nature of the metal counterions. Cu(II) is fully reduced to Cu(I) in **1** during the solvothermal reaction process.

The IR spectrum of **1**, **2**, and **3** showed strong and broad stretching bands centered at 3435, 3432, and 3434 cm^{-1}, respectively, which are attributed to the O–H stretching vibration for free or bonded waters. The IR spectrum of free 4-(4-hydroxyphenyl)-1,2,4-triazole showed two strong bands at 1531 and 1483 cm^{-1}, attributable to the triazole ring vibrations. Upon triazole coordination to metal ions, the bands are red-shifted by 19 and 28 wave numbers for Cu(I) (1550 and 1511 cm^{-1}), respectively. The strong bands centered at 1112, 1113, and 1116 cm^{-1} were assigned to ClO_4^- for **1**, **2**, and **3**, respectively [11].

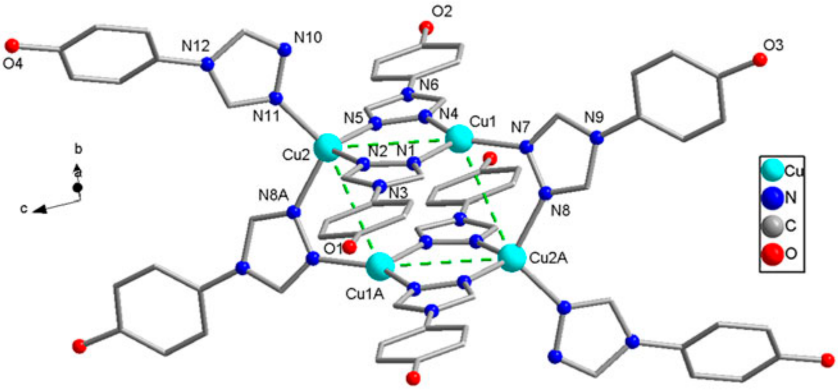


Figure 1. Perspective view of the tetranuclear cation of **1**. All lattice waters, ClO_4^-, and hydrogens have been omitted for clarity.

3.2. *Description of crystal structures*

3.2.1. $[Cu_4L_8](ClO_4)_4 \cdot 4H_2O$ (1). Single crystal X-ray analysis reveals that **1** crystallizes in triclinic space group $P\bar{1}$. The cluster consists of a tetranuclear Cu(I), eight L, four perchlorates and four waters. As shown in figure 1, Cu(1) is coordinated by three nitrogens (N1, N4, and N7) from three L ligands, leading to a trigonal geometry, while Cu(2) is surrounded by four nitrogens (N2, N5, N8A, and N11) from four different L ligands in a tetrahedral geometry. The Cu–N distances around Cu(1) and Cu(2) are 1.955(5)–2.039(6) and 2.004(5)–2.048(6) Å, respectively, which are similar to those found in the related Cu(I)–triazole complexes [12]. The N–Cu–N angles around Cu(I) centers range from 105.7(2)° to 138.9(3)° for Cu(1) and 104.5(2)° to 113.9(2)° for Cu(2), respectively, which are also in the normal range for Cu(I) complexes [12]. In **1**, there are two kinds of coordination modes for L, bidentate N1,N2-bridging coordination to bind Cu(1) and Cu(2) and monodentate coordination to Cu(2). Cu(1) and Cu(2) centers are linked by double N1,

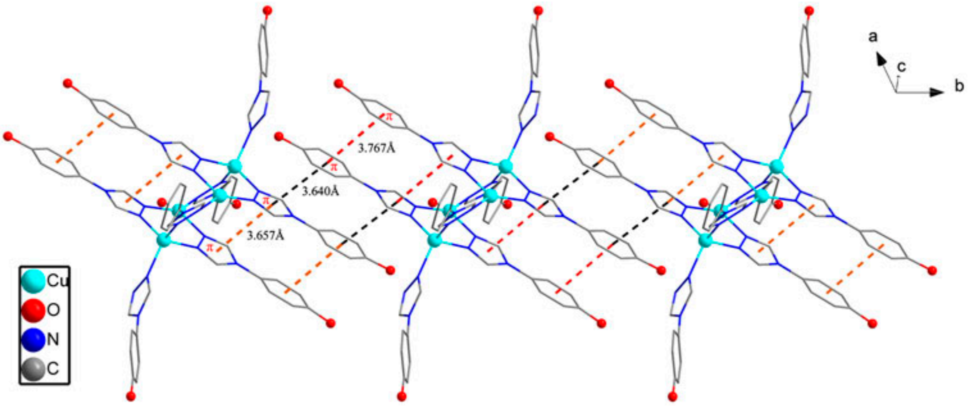


Figure 2. The 1D chain formed in **1** by $\pi \cdots \pi$ stacking interactions.

Table 3. Hydrogen bonding geometry (Å and °) for **1**–**3**.

D–H···A	D-H	H···A	D···A	∠D–H···A
Complex **1**				
O1–H1···O2$^{\#1}$	0.82	1.96	2.739(8)	158
O2–H2···N10$^{\#2}$	0.82	1.91	2.726(8)	174
O3–H3···O8A$^{\#3}$	0.82	1.99	2.81(2)	176
C1–H1A···O3$^{\#4}$	0.93	2.44	3.367(10)	174
C8–H8A···O3$^{\#4}$	0.93	2.59	3.462(11)	156
C13–H13A···O10A$^{\#2}$	0.93	2.62	3.376(5)	139
C15–H15A···O4A$^{\#5}$	0.93	2.41	3.179(12)	140
C25–H25A···O9B$^{\#6}$	0.93	2.56	3.47(2)	165
Complex **2**				
O1 W–H1WA···O2$^{\#7}$	0.85	1.98	2.820(8)	172
O2 W–H2WB···O5$^{\#8}$	0.884	2.536	3.303(11)	146
C1–H1A···O3$^{\#9}$	0.93	2.46	3.306(8)	151
C2–H2A···O5$^{\#10}$	0.93	2.40	3.286(8)	159
Complex **3**				
O1–H1A···O5$^{\#11}$	0.84	2.25	3.034(7)	154
O2–H2A···O6$^{\#12}$	0.85	2.01	2.819(7)	158
C7–H7···O4 $^{\#11}$	0.95	2.49	3.375(7)	155
C9–H9A···O6$^{\#13}$	0.98	2.59	3.463(8)	149

Note: Symmetry codes for **1**: (#1) $1+x, y-1, z$; (#2) $1-x, 1-y, 1-z$; (#3) $1+x, y, z-1$; (#4) $x, y, 1+z$; (#5) $x-1, y, z-1$; (#6) $2-x, 1-y, 1-z$. For **2**: (#7) $x-1, y, 1+z$; (#8) $1-x, -y, 2-z$; (#9) $1-x, -y, 1-z$; (#10) $1-z, 1-x, 1-y$. For **3**: (#11) $1/2-x, y, 1-z$; (#12) $1/2-x, 3/2-y, 1/2-z$; (#13) $1/2-x, 1/2+y, z$.

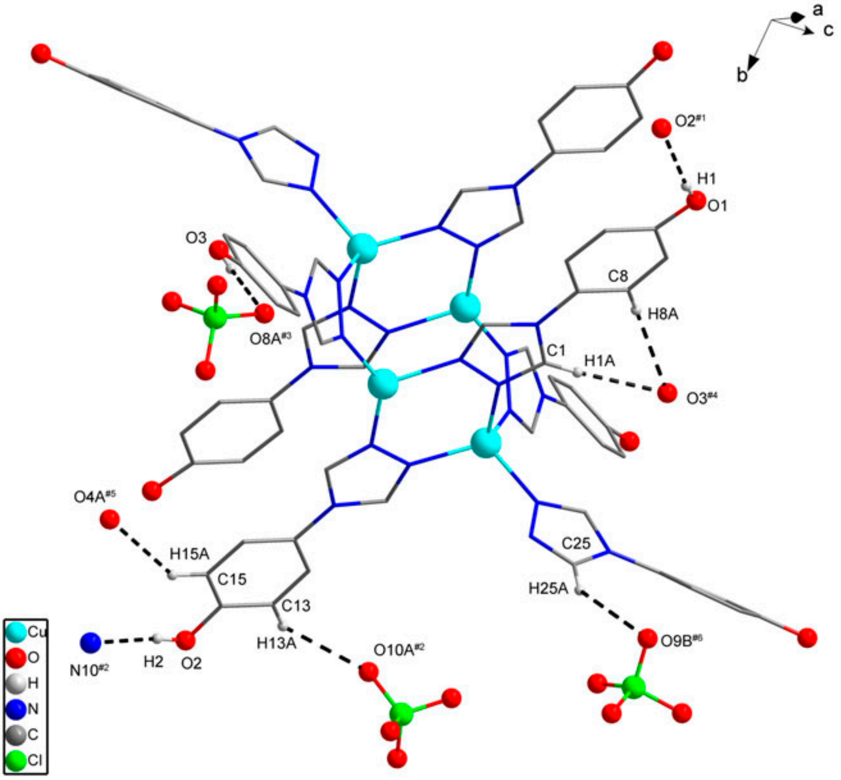


Figure 3. Hydrogen bonding interactions in **1**.

N2-bridges to form a six-membered ring [Cu(N1N2)$_2$Cu]. Each six-membered ring is further connected by two other ligands via N1,N2-bridges again to form a tetranuclear Cu(I) parallelogram. The distances of Cu(1)···Cu(2) and Cu(1)···Cu(2A) are 3.625(5) and 3.575(5) Å, respectively, and the angles of Cu(2A)–Cu(1)–Cu(2) and Cu(1)–Cu(2)–Cu(1A) are 110.6° and 69.4°, respectively. There are three kinds of strong offset face-to-face $\pi\cdots\pi$ interactions in **1**: (1) between the triazole ring with N1 and the triazole ring containing N4 with a distance of 3.657(5) Å and a dihedral angle of 6.4(4)°, (2) between the phenyl ring with C3 and the phenyl ring containing C11 with a distance of 3.767(5) Å and a dihedral angle of 3.5(4)°, and (3) between the triazole ring with N4 and the symmetry-related phenyl ring containing C11 with a distance of 3.640(5) Å and a dihedral angle of 4.3(4)°. These interactions link the molecules of **1** to form a 1-D chain along the *b* axis (figure 2) [5d-i]. There are eight kinds of hydrogen bond interactions in the structure of **1** (table 3 and figure 3).

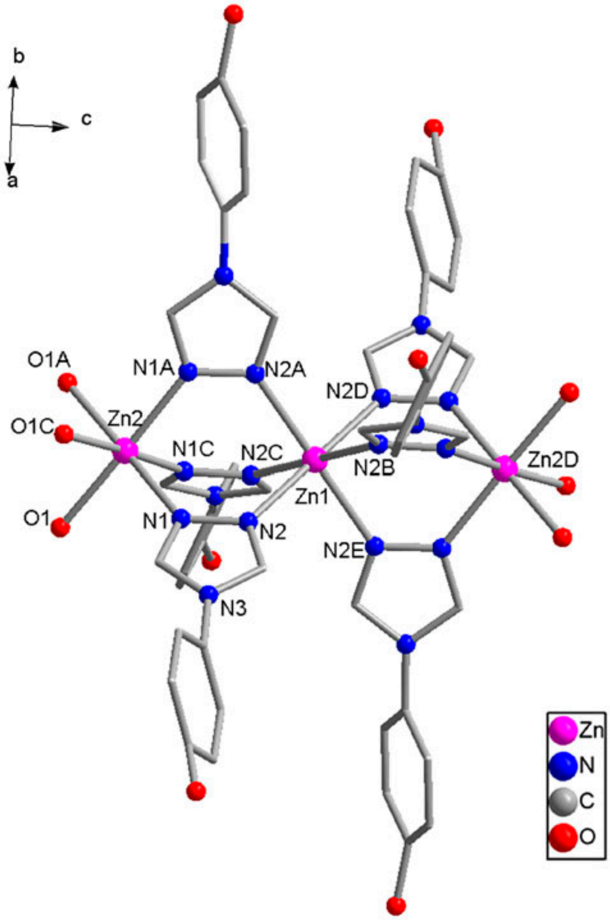


Figure 4. Perspective view of the trinuclear cation of **2**. All lattice waters, ClO_4^-, and hydrogens have been omitted for clarity.

3.2.2. $[Zn_3L_6(H_2O)_6](ClO_4)_6{\cdot}6H_2O$ (2) and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6{\cdot}4.5H_2O$ (3).

Complex **2** crystallizes in rhombohedral space group *R*-3, while **3** crystallizes in cubic space group *Ia*-3. Complex **2** consists of a linear trinuclear cation with a + 6 charge, six perchlorates, and six lattice waters. Complex **3** consists of a linear trinuclear cation with a + 6 charge, six perchlorates, and four-and-a-half lattice waters. The central Zn(II) in **2** presents a distorted octahedral geometry, defined by six nitrogens (N1, N1A, N1B, N1C, N1D, and N1E) from six different ligands (figure 4). The ligand–metal–ligand bite angles around Zn1 slightly differ from the ideal value of 90°, varying from 89.25(12)° to 90.25(12)°. Each external Zn(II) completes its octahedral surroundings with three waters and three nitrogens (N2, N2A, and N2C). The Zn–N distances are in the normal range and the average distance of the central Zn–N is 0.061 Å longer than the terminal [Zn_{center}–N = 2.180(3) Å and $Zn_{terminal}$–N = 2.119(3) Å] [13]. The difference in bond lengths is attributed to steric hindrance [14]. The central Zn1 lies on the inversion center and is triply bridged to each of the external Zn2 ions by the ligands through the nitrogens in the 1,2-positions. The triazole in **2** displays a bidentate N1,N2-bridging coordination to form a six-membered ring [Zn $(N1N2)_2$Zn] with Zn1···Zn2 distance of 3.853(5) Å. The structure of **3** is very similar to **2**,

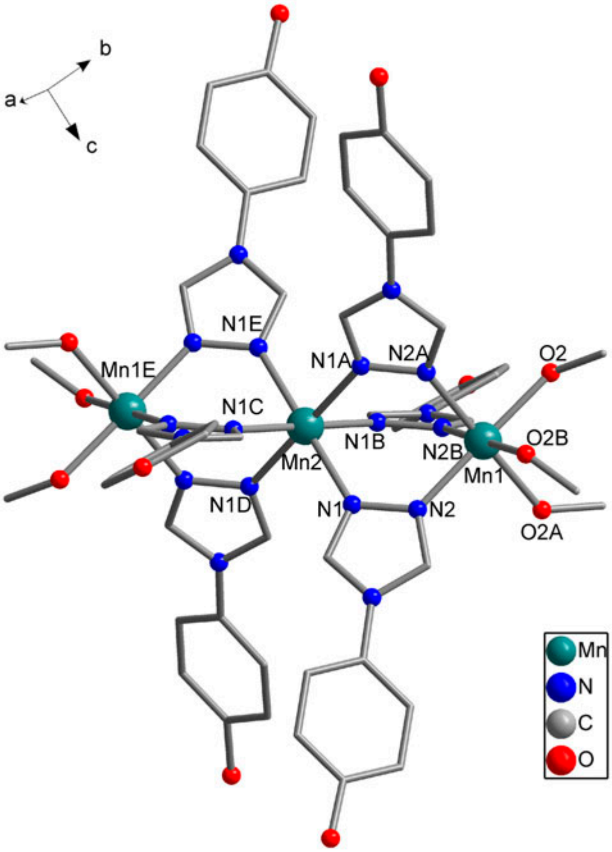


Figure 5. Perspective view of the trinuclear cation of **3**. All lattice waters, ClO_4^-, and hydrogens have been omitted for clarity.

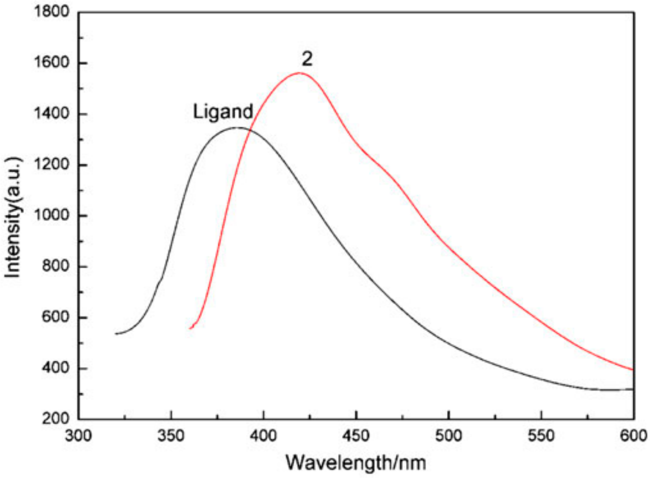


Figure 6. Solid-state fluorescent spectra for L and **2**.

however, the external Mn(II) in **3** is coordinated by three MeOH molecules (figure 5). In addition, four kinds of hydrogen bond interactions are observed in **2** and **3** (table 3).

3.3. *Luminescent properties*

The solid-state emission spectra of **2** were measured at room temperature (figure 6). Complex **2** exhibits a strong fluorescent emission band at ca. 448 nm with $\lambda_{ex} = 368$ nm. The free 4-(4-hydroxyphenyl)-1,2,4-triazoles (L) exhibited weak fluorescent emission band at ca. 401 nm upon excitation at ca. 342 nm. As compared with the emission spectrum of L, the red shift of 47 nm in **2** is observed. As a result, the emission peak of **2** can be ascribed to the emission of ligand-to-metal charger-transfer which is in reasonable agreement with that found in reported Zn(II) complexes [15]. Complexes **1** and **3** do not exhibit detectable emission.

4. Conclusion

Some complexes containing a triazole ligand $\{[Zn(Hbtc)(bmt)]\cdot DMF\cdot 5H_2O\}_n$ (H_3btc = 1,3,5-benzenetricarboxylic acid, bmt = 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole), $\{[Cu(trzp)_2(H_2O)]\cdot 1.18H_2O\}_n$, $\{[Co(trzp)_2(H_2O)_2]\cdot 2H_2O\}_n$, $\{[Cd(trzp)_2(H_2O)]\cdot 2H_2O\}_n$ (trzp = 1*H*-1,2,4-triazole-1-propionic acid) and $[Cu(bte)(H_2btc)_2]_n$ (bte = bis(1,2,4-triazol-1-yl)ethane) have been reported [16]. By the use of 4-(4-hydroxyphenyl)-1,2,4-triazole (L) as the ligand, three complexes, $[Cu_4L_8](ClO_4)_4\cdot 4H_2O$ (**1**), $[Zn_3L_6(H_2O)_6](ClO_4)_6\cdot 6H_2O$ (**2**), and $[Mn_3L_6(CH_3OH)_6](ClO_4)_6\cdot 4.5H_2O$ (**3**) have been synthesized by hydrothermal reactions. The structure of **1** is different from $[(CuL)_2(\mu\text{-}NC)_2Mo^{IV}(CN)_6]$ (H_2L = binucleating Schiff-base with the 1-D coordination polymer [17]. The structure of **2** is different from $[Zn_4L_2(OAc)_2(CH_3OH)_2]$ (H_3L = 6-hydroxy-4′,6′-dibromo-2,2′-[ethylenediyldioxybis(nitrilomethylidyne)]diphenol) with a tetranuclear structure [18]. The structural features exhibited by **1**–**3** showed the diverse modes of the triazole groups. Variation of the coordination modes of the flexible ligands as well as the reaction conditions leads to the formation of complexes with different structures. Furthermore, **2** exhibited luminescent properties at room temperature in the solid state.

Supplementary material

CCDC 869994, 869995, and 876348 contain the supplementary crystallographic data for **1**, **2**, and **3**. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center. Copies of this information can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; Email: deposit@ccdc.ac.uk).

Funding

This work was supported by the Natural Science Fund of Jiangsu Province of PR China [grant number BK2012643], [grant number 12KJA150001], NSFC [grant number 21001018], [grant number 21171093], [grant number 21201025] and the start-up grant from CSLG [grant number KYZ2010131Z].

Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2014.927060].

References

[1] (a) J.G. Haasnoot. *Coord. Chem. Rev.*, **200**, 131 (2000); (b) G. Christou. *Acc. Chem. Res.*, **22**, 328 (1989); (c) S. Hill, R.S. Edwards, N. Aliaga-Alcalde, G. Christou. *Science*, **302**, 1015 (2003); (d) R. Bagai, G. Christou. *Chem. Soc. Rev.*, **38**, 1011 (2009); (e) D. Gatteschi, R. Sessoli. *Angew. Chem. Int. Ed.*, **42**, 268 (2003).
[2] T. Asaji, H. Sakai, D. Nakamura. *Inorg. Chem.*, **22**, 202 (1983)
[3] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Muller, M.B. Cingi, M. Lanfranchi, A.M. Lanfredi, J. Ribas. *Inorg. Chem.*, **39**, 1859 (2000).
[4] O.G. Shakirova, A.V. Virovets, D.Yu. Naumov, Y.G. Shvedenkov, V.N. Elochina, L.G. Lavrenova. *Inorg. Chem. Commun.*, **5**, 690 (2002).
[5] (a) D.R. Zhu, Y. Song, Y. Xu, Y. Zhang, H.K. Fun, X.Z. You. *Polyhedron*, **19**, 2019 (2000); (b) D. Zhu, Y. Xu, Z. Yu, Z. Guo, H. Sang, T. Liu, X. You. *Chem. Mater.*, **14**, 838 (2002); (c) J. Yang, W.W. Bao, X.M. Ren, X. Shen, D.R. Zhu. *J. Coord. Chem.*, **62**, 1809 (2009); (d) G.P. Shen, J. Zhao, J.J. Jiang, Q. Liu, X. Shen, Y. Xu, D.R. Zhu, X.Q. Liu. *J. Mol. Struct.*, **1002**, 159 (2011); (e) L. Chen, J. Zhao, G.P. Shen, X. Shen, Y. Xu, D.R. Zhu, J. Wang. *J. Coord. Chem.*, **64**, 3980 (2011); (f) J. Zhao, H.M. Cheng, G.P. Shen, Y. Xu, D.R. Zhu. *J. Coord. Chem.*, **64**, 942 (2011); (g) L. Wang, J.J. Jiang, L. Chen, X. Shen, D.R. Zhu. *Inorg. Chem. Commun.*, **28**, 104 (2013); (h) G.P. Shen, L. Qi, L. Wang, Y. Xu, J.J. Jiang, D.R. Zhu, X.Q. Liu, X. You. *Dalton Trans.*, 10144 (2013); (i) J. Gong, X. He, L. Chen, X. Shen, D.R. Zhu. *J. Coord. Chem.*, **66**, 2875 (2013).
[6] E.V. Lider, E.V. Peresypkina, A.I. Smolentsev, V.N. Elokhina, T.I. Yaroshenko, A.V. Virovets, V.N. Ikorskii, L.G. Lavrenova. *Polyhedron*, **26**, 1612 (2007).
[7] J. Yang, Y.S. Ma, X.Y. Tang, L. Shen, R.X. Yuan, D.R. Zhu. *J. Coord. Chem.*, **64**, 3291 (2011).
[8] R.H. Wiley, A.J. Hart. *J. Org. Chem.*, **18**, 1368 (1953).
[9] Rigaku Crystal Clear, Rigaku Corporation, Tokyo, Japan (2005).
[10] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[11] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*, p. 86, Wiley, New York, NY (2009).

[12] (a) X. He, C.Z. Lu, C.D. Wu, L.J. Chen. *Eur. J. Inorg. Chem.*, **2006**, 2491 (2006); (b) W. Ouellette, A.V. Prosvirin, V. Chieffo, K.R. Dunbar, B. Hudson, J. Zubieta. *Inorg. Chem.*, **45**, 23 (2006).
[13] (a) Z. Li, L. Mian, X.-P. Zhou, T. Wu, D. Li, S.W. Ng. *Cryst. Growth Des.*, **7**, 1992 (2007); (b) T. Jiang, X.-M. Zhang. *Cryst. Growth Des.*, **8**, 3077 (2008); (c) R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z. Xue. *Angew. Chem. Int. Ed.*, **41**, 20 (2002).
[14] B. Liu, L. Xu, G.-C. Guo, J.-S. Huang. *J. Mol. Struct.*, **825**, 79 (2006).
[15] (a) H.F. Zhu, Z.H. Zhang, T.A. Okamura, W.Y. Sun, N. Ueyama. *Cryst. Growth Des.*, **5**, 177 (2005); (b) Z.Y. Fu, X.T. Wu, J.C. Dai, S.M. Hu, W.X. Du, H.H. Zhang, R.Q. Sun. *Eur. J. Inorg. Chem.*, **2002**, 2730 (2002); (c) J. Tao, M.L. Tong, J.X. Shi, X.M. Chen, S.W. Ng. *Chem. Commun.*, 2043 (2000).
[16] (a) B.T. Liu, R. Wang, G.H. Jin, X.R. Meng. *J. Coord. Chem.*, **66**, 1784 (2013). L. Tian, S.Y. Zhou. *J. Coord. Chem.*, **66**, 2863 (2013); (b) Z. Zhang, D.F. Wu, K. Hu, Y.J. Shi, Z.L. Chen, F.P. Liang. *J. Coord. Chem.*, **66**, 2499 (2013).
[17] (a) Q. Zhang, F.P. Huang, H.D. Bian, Q. Yu. *J. Coord. Chem.*, **64**, 2110 (2011); (b) D. Visinescu, J.P. Sutter, C. Duhayon, A.M. Madalan, B. Jurca, M. Andruh. *J. Coord. Chem.*, **64**, 93 (2011).
[18] W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Cha, X.H. Gao. *J. Coord. Chem.*, **65**, 1212 (2012).