Ж У Р Н А Л   С Т Р У К Т У Р Н О Й   Х И М И И

2013. Том 54, № 4 *Июль – август* *С. 759 –762*

КРАТКИЕ СООБЩЕНИЯ

UDC 541.6:547.13:546.47

HYDROTHERMAL SYNTHESIS, CRYSTAL STRUCTURE, AND LUMINESCENCE OF A NOVEL TETRANUCLEAR ZINC(II) COMPLEX

J. Wang, J.-Q. Tao, X.-J. Xu, C.-Y. Tan

Department of Chemistry, Yancheng Teachers' College, Yancheng, Jiangsu, P.R. China
E-mail: wjyctu@gmail.com

Received February, 23, 2012

A new tetranuclear zinc(II) complex $[Zn_4(tmphen)_4(tbip)_4(H_2O)_4]$ (**1**, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline, H_2tbip = 5-*tert*-butyl isophthalic acid) is hydrothermally synthesized and structurally characterized by single crystal X-ray diffraction, elemental analysis, and IR spectroscopy. In complex **1**, four $tbip^{2-}$ ligands act as bridges between four neighboring Zn atoms to form an unusual tetranuclear zinc cluster. The clusters are further connected by two types of O—H···O and C—H···O hydrogen bonds, generating a three-dimensional supramolecular structure. Meanwhile, π—π stacking interactions and C—H···π interactions further consolidate the three-dimensional supramolecular framework of **1**. In addition, the luminescence measurements reveal that complex **1** exhibits strong fluorescent emissions in the solid state at room temperature.

Keywords: tetranuclear, 3,4,7,8-tetramethyl-1,10-phenanthroline, 5-*tert*-butyl isophthalic acid and fluorescent property.

The design and synthesis of coordination polymers is an attractive area of research not only due to their intriguing structures but also their potential applications in optics, magnetism, gas storage, ion exchange, catalysis, etc. [1—3]. The most effective and facile approach to coordination polymers is to utilize multi-pyridine and dicarboxylate ligands to link metal ions, giving infinite frameworks [4—6].

Owing to an excellent coordination ability and a large conjugated system, 1,10-phenanthroline (phen) has been widely used to build coordination polymers [7, 8]. Since carboxylate groups have an excellent coordination ability and flexible coordination patterns, isophthalic acid has also been widely used in the construction of metal-organic frameworks [9, 10]. However, relatively less attention has been paid to their derivatives. Here, we selected 5-*tert*-butyl isophthalic acid (H_2tbip) as an organic linker and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) as an N-donor chelating ligand, generating a new Zn(II) coordination complex $[Zn_4(tmphen)_4(tbip)_4(H_2O)_4]$ **1**.

Experimental. All reagents and solvents were commercially available and used without further purification. The IR spectra were obtained within the 400—4000 cm^{-1} as KBr disks on a VECTOR 22 spectrometer. Elemental analyses (C, H, and N) were performed on a Perkin Elmer 240C elemental analyzer. An emission spectrum was recorded on a Hitachi F-4500 fluorescence spectrophotometer, using a slit width of 5 nm excitation at room temperature for the solid samples.

Synthesis of $[Zn_4(tmphen)_4(tbip)_4(H_2O)_4]$. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol), Tmphen (0.0236 g, 0.1 mmol), H_2tbip (0.0222 mg, 0.1 mmol), and KOH (0.0112 g, 0.2 mmol) in H_2O (10 ml) was sealed in a 16 ml. Teflon-lined stainless steel container and heated at 180 °C for 72 h. After cooling to room temperature, white block crystals were collected by filtration and washed by water and ethanol several times (yield 41.7 %, based on H_2tbip).

© Wang J., Tao J.-Q., Xu X.-J., Tan C.-Y., 2013

Table 1

Crystal data and structure refinement for complex **1**

1			
Formula	$Zn_4C_{112}H_{120}N_8O_{20}$	ρ_{calcd}, g/cm^3	1.439
M	2159.73	μ(MoK_α), mm^{-1}	1.028
System	Triclinic	Crystal size, mm	0.21×0.18×0.15
Space group	$P\overline{1}$	θ range, deg.	2.10—25.50
a, b, c, Å	11.027(4), 13.149(5), 18.364(7)	F(000)	1128
α, β, γ, deg.	95.268(5), 94.065(5), 109.075(4)	$R_1{}^a$ $[I > 2\sigma(I)]$	0.0540
V, Å^3	2491.4(16)	$wR_2{}^b$ $[I > 2\sigma(I)]$	0.1037
Z	1	GOOF	0.865

For $C_{112}H_{120}Zn_4N_8O_{20}$ anal. calcd, %: C, 62.28; H, 5.60; N, 5.19. Found, %: C, 62.46; H, 5.64; N, 5.21. IR bands (ν, cm^{-1}): 1427 ν$(OCO)_{sym}$, 1680 ν$(OCO)_{assym}$, 3412 $\nu_b(H_2O)$.

X-ray crystallography. The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK_α radiation (λ = 0.71073 Å) at 295 K. Absorption correction was performed using the SADABS program [11]. The structure was solved by a direct method using the SHELXL-97 program [12] and refined by the full-matrix least-squares technique on F^2 with SHELXL-97. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystal data collection and refinement parameters are given in Table 1. CCDC reference number is 843515.

Results and discussion. The structure of complex **1** features a centrosymmetric tetranuclear Zn(II) cluster unit. As shown in Fig. 1, complex **1** crystallizes in the triclinic space group $P\overline{1}$ with an asymmetric unit comprising two crystallographically distinct divalent zinc atoms (Zn1, Zn2), two doubly deprotonated bridging tbip dianions (type A, O1—O4; type B, O7—O10), two tmphen chelating ligands (type C, N1—N2; type D, N3—N4) and two coordinated water molecules. The Zn1 atom bonds to two carboxylate oxygen atoms (O1, O7) from two different tbip^{2-} ligands, two nitrogen atoms (N(1) and N(2)) from one chelating tmphen ligand, and one water oxygen atom (O5) in a distorted $\{ZnO_3N_2\}$ square pyramid. The coordination environment of the Zn2 atom is completed by two carboxylate oxygen atoms (O3, O9^i (i = $-x$+1, $-y$+1, $-z$+1)) from two distinct tbip^{2-} ligands, two nitrogen

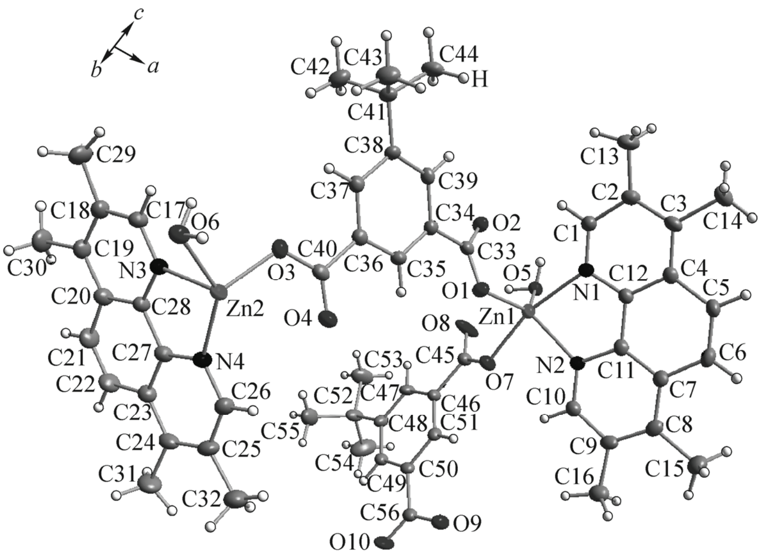
Table 2

Selected bond distances (Å) *and angles* (deg.) *for* **1**

Zn(1)—O(1)	1.955(3)	O(1)—Zn(1)—O(5)	126.56(12)	O(1)—Zn(1)—O(7)	93.69(12)
Zn(1)—O(7)	2.061(3)	O(1)—Zn(1)—N(2)	118.30(14)	O(5)—Zn(1)—N(2)	115.12(12)
Zn(1)—N(2)	2.101(4)	O(1)—Zn(1)—N(1)	93.93(13)	O(5)—Zn(1)—N(1)	96.49(12)
Zn(2)—O(6)	2.098(3)	N(2)—Zn(1)—N(1)	76.71(13)	O(3)—Zn(2)—O(9)#1	117.15(12)
Zn(2)—N(3)	2.182(4)	O(9)#1—Zn(2)—O(6)	89.23(12)	O(3)—Zn(2)—N(4)	119.16(13)
Zn(1)—O(5)	2.008(3)	O(6)—Zn(2)—N(4)	141.71(12)	O(3)—Zn(2)—N(3)	102.74(13)
Zn(1)—N(1)	2.172(3)	O(6)—Zn(2)—N(3)	85.31(12)	N(4)—Zn(2)—N(3)	75.45(14)
Zn(2)—O(3)	1.932(3)	O(5)—Zn(1)—O(7)	89.63(12)	O(3)—Zn(2)—O(6)	97.04(11)
Zn(2)—O(9)#1	1.986(3)	O(7)—Zn(1)—N(2)	87.93(12)	O(9)#1—Zn(2)—N(4)	85.13(13)
Zn(2)—N(4)	2.111(3)	O(7)—Zn(1)—N(1)	164.63(13)	O(9)#1—Zn(2)—N(3)	140.11(13)

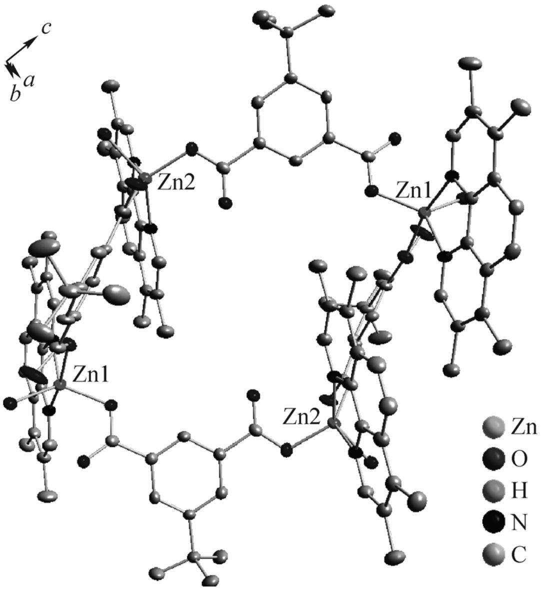
#1 $-x$+1, $-y$+1, $-z$+1.

Fig. 1. ORTEP view of asymmetric unit for complex **1**, displacement ellipsoids are drawn at the 30 % probability level



atoms (N3 and N4) from another chelating tmphen ligand, and one water oxygen atom (O6) in a distorted square pyramid geometry. The Zn—O$_{\text{carboxylate}}$ bond lengths range from 1.932(3) Å to 2.061(3) Å; the Zn—O$_{\text{aqua}}$ bond lengths vary from 2.008(3) Å to 2.098(3) Å, and the Zn—N bond lengths are from 2.101(4) Å to 2.182(4) Å; all are comparable to the corresponding values found in other Zn(II) complexes [13—15]. Adjacent Zn1 and Zn2 atoms are joined into neutral tetranuclear zinc(II) complex by bis-(monodentate) tbip ligands (Fig. 2). The Zn1···Zn2 contact distances through the crystallographically distinct tbip ligands are 9.706 Å and 7.833 Å. These differences are provided by conformational variances within the distinct tbip ligands. In tbip-A, the carboxylate groups are twisted by 26.6°, 9.7° relative to the plane of the phenyl ring. The related torsions in tbip-B are 9.7°, 7.5°. The Zn1···Zn1 and Zn2···Zn2 through-space distances across the tetranuclear kernel measure 14.009 Å and 10.718 Å respectively. These rhomboid units are noticeably pinched with Zn1—Zn2—Zn1 and Zn2—Zn1—Zn2 angles of ~105.5° and ~74.5° respectively.

There are extensive inter- and intramolecular hydrogen bonds of O—H···O and C—H···O types connecting the tetranuclear structure of complex **1**. O(5)—H(5B)···O(8), C(1)—H(1)···O(2), C(10)—H(10)···O(7), C(32)—H(32B)···O(1)^{i}, and C(37)—H(37)···O(3) are intramolecular hydrogen bonding interactions. The molecules of complex **1** are linked with each other through O(5)—H(5A)···O(2)^{ii}, O(6)—H(6A)···O(10)^{iii}, O(6)—H(6B)···O(3)^{iv}, C(5)—H(5)···O(5)^{v}, C(13)—H(13C)···(8)^{vi}, C(17)—H(17)···O(10)^{iii}, C(21)—H(21)···O(4)^{iv}, and C(29)—H(29A)···O(10)^{iv} ($i = -x+1, -y+1, -z+1$; $ii = -x+1, -y+1, -z+2$; $iii = x-1, y-1, z$; $iv = -x, -y, -z+1$; $v = -x+2, -y+1, -z+2$) hydrogen bonding interactions to construct a 3D supramolecular architecture (Fig. 3). In addition, the C—H···π interaction is



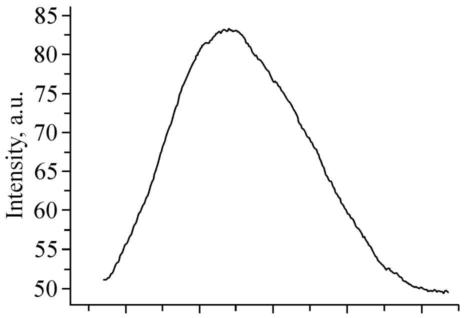


Fig. 2 (*left*). View of the tetranuclear zinc(II) complex

Fig. 3 (*right*). Solid-state emission spectrum of complex **1** at room temperature observed between C16—H16C and the centroid (C*g*) of the C20—C21—C22—C23—C27—C28 phenyl ring, with C16···C*g* = 3.405(6) Å, H16C···C*g* = 2.62 Å and C16—H16C···C*g* = 140°. Another C—H···π interaction exists between C31—H31C and the centroid (Cg) of the N2—C7—C8—C9—C10—C11 pyridine ring with C31···C*g* = 3.700(6) Å, H31C···C*g* = 2.88 Å and C31—H31C···C*g* = = 144°. Furthermore, the π···π stacking interactions between the molecules of complex **1** are observed with the centroid-to-centroid distance in the range of 3.598(3)—3.699(3) Å, which increase ulteriorly the stability of the 3D supramolecular architecture of **1**.

The IR spectrum of complex **1** shows a strong and broad absorption peak at 3412 cm^{-1} which is attributable to the O—H stretching vibrations of bonded water molecules. The strong vibrations appearing around 1680 cm^{-1} and 1427 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the carboxylate group respectively. The $\Delta\nu$ ($\nu(OCO)_{assym} - \nu(OCO)_{sym}$) is 253 cm^{-1} (>200), showing the presence of a monodentate linkage of carboxylates in the dianions. The absence of strong absorption bands around 1700 cm^{-1} indicates that the ligands are deproponated, which is in agreement with the X-ray structure [16].

The fluorescent property of complex **1** was studied in the solid state at room temperature. The free ligands exhibit emissions at 324 nm for H$_2$tbip [17]. The emission bands of the free ligands are probably caused by the π*—*n* or π*—π transition. Irradiation of crystalline samples of complex **1** with ultraviolet light (k_{ex} = 375 nm) caused moderately intense emission with k_{max} values of 351 nm. (Fig. 3). According to a recent review of d^{10} metal coordination polymer luminescence [18], the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions.

In summary, using 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen), 5-*tert*-butyl isophthalic acid (H$_2$tbip), KOH, and Zn(NO$_3$)$_2$·6H$_2$O, we isolated a new tetranuclear zinc(II) complex [Zn$_4$(tmphen)$_4$(tbip)$_4$(H$_2$O)$_4$] that was characterized by single crystal X-ray diffraction, elemental analysis, and IR spectroscopy. In addition, complex **1** exhibits strong fluorescence emissions in the solid state at room temperature.

Acknowledgements. This work was supported by the Natural Science Fund for colleges and universities in Jiangsu Province (No. 11KJD150006).

REFERENCES

1. *Ferey G., Mellot-Draznieks C., Serre C. et al.* // Acc. Chem. Res. – 2005. – **38**. – P. 217.
2. *Kitagawa S., Kitaura R., Noro S.* // Angew. Chem. Int. Ed. – 2004. – **43**. – P. 2334.
3. *Eddaoudi M., Moler D.B., Li H. et al.* // Acc. Chem. Res. – 2001. – **34**. – P. 319.
4. *Wu M.-F., Wang M.-S., Guo S.-P. et al.* // Crystal Growth & Design. – 2011. – **11**. – P. 372.
5. *Su Z., Fan J., Okamura T. et al.* // Crystal Growth & Design. – 2010. – **10**. – P. 3515.
6. *Ma L.-F., Li X.-Q., Meng Q.-L. et al.* // Crystal Growth & Design. – 2011. – **11**. – P. 175.
7. *Bi W., Cao R., Sun D. et al.* // Chem. Commun. – 2004. – P. 2104.
8. *Zheng Y.-Z., Liu G.-F., Ye B.-H. et al.* // Z. Anorg. Allg. Chem. – 2004. – **630**. – P. 296.
9. *Tao J., Chen X.-M., Huang R.-B. et al.* // Journal of Solid State Chemistry. – 2003. – **170**. – P. 130.
10. *Shi X., Zhu G.,Wang X. et al.* // Crystal Growth & Design. – 2005. – **5**. – P. 341.
11. *Sheldrick G.M.* SADABS An empirical absorption correction program, Madison, WI, Bruker Analytical X-ray Systems, 1996.
12. *Sheldrick G.M.* SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
13. *Chen S.-Y., Guo Y.-C., Yan J.-W. et al.* // Chinese J. Struct. Chem. – 2010. – **29**. – P. 676.
14. *Lu R.Y., Han Z.B.* // Russ. J. Coord. Chem. (Engl. Transl.). – 2011. – **37**, N 3. – P. 172.
15. *Gao E.J., Guo M.J., Zhang Y.X. et al.* // Russ. J. Coord. Chem. (Engl. Transl.). – 2010. – **36**, N 12. – P. 923.16.
16. *Nakamoto K.* Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th edn. Part B, John Willey, New York, 1997.
17. *Ma L.-F., Wang Y.-Y., Liu J.-Q., Yang G.-P. et al.* // CrystEngComm. – 2009. – **11**. – P. 1800.
18. *Allendorf M.-D., Bauer C.-A., Bhakta R.-K. et al.* // Chem. Soc. Rev. – 2009. – **38**. – P. 1330.