ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 7, pp. 447–450. © Pleiades Publishing, Ltd., 2015.

Synthesis, Crystal Structure, and Fluorescent Property of $[Zn^{II}(Pta)_2(4,4'\text{-}Bipy)(H_2O)_2]_n$[1]

C. L. Ma, J. Wu, and Y. F. Chen*

School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan, 430073 P.R. China

**e-mail: chyfch@hotmail.com*

Received November 17, 2014

Abstract—A coordination polymer of $[Zn^{II}(Pta)_2(4,4'\text{-}Bipy)(H_2O)_2]_n$ (HPta = 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetic acid, 4,4'-Bipy = 4,4'-bipyridine) was synthesized and characterized by IR, fluorescence spectroscopy and X-ray single crystal diffraction (CIF file CCDC no. 1001498). The complex crystallizes in triclinic, space group $P\overline{1}$ with $a = 5.574(2)$, $b = 11.514(5)$, $c = 12.140(5)$ Å, $\alpha = 64.653(6)°$, $\beta = 86.859(8)°$, $\gamma = 84.282(7)°$, $V = 700.6(5)$ Å^3, $\rho_c = 1.569$ g/cm^3, $Z = 1$, $C_{30}H_{28}N_8O_6Zn$, $Mr = 661.97$, $F(000) = 342$, $\mu = 0.938$ mm^{-1}, the final $R = 0.0578$ and $wR = 0.1241$ for 4876 observed reflections with $I > 2\sigma(I)$. In this complex, the 1,2,3-triazole-carboxylic acid ligand, which only supplies a carboxylic anion to coordinate with Zn^{2+} ions, while the nitrogen atoms of 1,2,3-triazole don't coordinate with Zn^{2+} ions, the 4,4'-bipyridine ligand serves as a linker to form a 1D chain structure, the abundant hydrogen bonding which plays an important role in forming 2D structure. Compared with free HPta and 4,4'-Bipy, the intensity of fluorescence of Pta with $Zn(OAc)_2$ and 4,4'-Bipy with $Zn(OAc)_2$ enhanced. However, the complex displays fluorescence quenching, which probably be caused by charge transfer which due to HPta and 4,4'-Bipy mutual coordination with Zn(II).

DOI: 10.1134/S1070328415070064

INTRODUCTION

With the development of the Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) reaction [1], the 1,2,3-triazole has become a popular building block in many fields, such as pharmaceutical research [2], materials chemistry [3] and bioconjugation [4]. More recently, the 1,2,3-triazoles also served as ligand to form the 1,2,3-triazole-based metal complexes with different metals, such as Cu [5], Zn [6], Co [7], Ni [8], Pd [9], etc. [10], some of them show unique properties. For the abundant coordination nitrogen atoms and high electron density of the 1,2,3-triazole ring together with their strong stability, the 1,2,3-triazoles can be a good candidate ligand for the synthesis of new metal complexes.

At the same time, 4,4'-bipyridine (4,4'-Bipy), which is a rigid bidentate spacer, has been extensively used as bridging group along with proper metal ions resulting in conjugation with other co-ligands [11]. Mostly, complexes bridged by 4,4'-Bipy have interesting supra-molecular architectures owing to its coordination interactions [12]. In this paper, we synthesized a Zn(II) coordination polymer $[Zn^{II}(Pta)_2(4,4'\text{-}Bipy)(H_2O)_2]_n$ (**I**) by the mixing the 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetic acid (HPta) and 4,4'-Bipy ligand with the $Zn(OAc)_2$ under the hydrothermal condition. The fluorescence properties of the complex and free ligands were investigated, the results revealed that the fluorescence quenching occurred for this complex (the fluorescence enhancement for Zn(II) with single free ligands), which probably be caused by the HPta and 4,4'-Bipy mutual coordination with Zn(II).

EXPERIMENTAL

Materials and physical measurement. All chemicals were purchased from commercial available and used without further purification. FT-IR spectrum was recorded from KBr pellets and the range of 500–4000 cm^{-1} on a Nicolet IS50-IR spectrometer. ^{1}H NMR spectra were recorded on Varian Mercury 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (TMS) (0.00 ppm) or DMSO-d_6 (2.50 ppm) for ^{1}H NMR. Melting points were measured on a melting point tester RY-1G apparatus. The liquid-state fluorescence emission/excitation spectra were recorded on a Hitachi F-7500 fluorescence spectrophotometer equipped with a continuous Xe-900 xenon lamp and a μF900 microsecond flash lamp. Crystal determination was performed with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å), structure were solved by direct method using SHELXL program and

---

[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	5.574 (2)
b, Å	11.514(5)
c, Å	12.140(5)
α, deg	64.653(6)
β, deg	86.859(8)
γ, deg	84.282(7)
V, Å^3	700.6(5)
Z	1
ρ_{calcd}, g cm^{-3}	1.569
Crystal size, mm	0.1 × 0.1 × 0.1
F(000)	342
μ(MoK_α), mm^{-1}	0.938
θ Range for data collection, deg	1.86–24.99
Index range h, k, l	$-6 \le h \le 6$, $-13 \le k \le 13$, $-14 \le l \le 14$
Type of scan	Multi-scan
Reflections collected	4876
Independent reflections, R_{int}	0.0591
Reflections with $I > 2\sigma$, I	0.1241
Number of refinement parameters	2423
Goodness-of-fit on F^2	1.055
Final R_1, wR_2, $I > 2\sigma$, (I)*	$R_1 = 0.0578$, $wR_2 = 0.1241$
R_1, wR_2, all data**	$R_1 = 0.0814$, $wR_2 = 0.1390$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.774, –0.367

* $R = \Sigma(F_o - F_c)/\Sigma(F_o)$, ** $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^2)^2\}^{1/2}$.

refined by full-matrix least squares on F^2. Power X-ray diffraction (PXRD) was recored on Bruker D8-ADVANCEX with CuK_α radiation ($\lambda = 1.5418$ Å).

Synthesis of I. The HPta was synthesized according to the literature [13]. A mixture of ethynylbenzene (0.102 g, 1 mmol), 2-azidoacetic acid (0.121 g, 1.2 mmol) were treated with $CuSO_4 \cdot 5H_2O$ (0.013 mg, 0.05 mmol) and sodium ascorbate (0.029 g, 0.15 mmol) in MeOH (8 mL). A white solid (0.153 g, 0.76 mmol) was obtained. Its melting point is 197–199°C and chemistry shifts of ^{1}H NMR (400 MHz, DMSO) are 13.01 (s., 1H), 8.57 (s., 1H), 7.88 (m., 2H), 7.40 (s., 2H), 7.34 (s., 1H), 5.38 (s., 2H) ppm, which are consistent with the literature reports.

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.066 g, 0.3 mmol), 4,4'-Bipy (0.021 g, 0.10 mmol), HPta (0.040 g, 0.1 mmol), H_2O (7 mL) was placed in a 23 mL Teflon-lined autoclave. The vessel was heated to 120°C for 24 h, and then cooled to room temperature. Colorless block crystals were obtained.

For $C_{30}H_{28}N_8O_6Zn$

anal. calcd., %:	C, 59.11;	H, 20.68;	N, 4.46.
Found, %:	C, 59.04;	H, 20.89;	N, 4.54.

IR (KBr, ν, cm^{-1}): 3249, 1612, 1458, 1294, 1167, 1035, 971, 805, 761, 686, 622.

X-ray structure determination. A colorless single crystal of complex **I** was determined with MoK_α radiation using a BRUKER SMART APEX II CCD diffractometer at 296(2) K using the ω–2θ scan mode. In the range of 2.12° ≤ θ ≤ 26.00°, a total of 35305 reflections were obtained with 9983 unique ones and used in the succeeding refinements. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXL-97 [14]. The crystal data as well as details of data collection and refinements for the complex are listed in Table 1. The selected bond lengths and bond angles of the title complex are listed in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1001498; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The ORTEP drawing of the compound with atom labeling is shown in Fig. 1. The extended structure

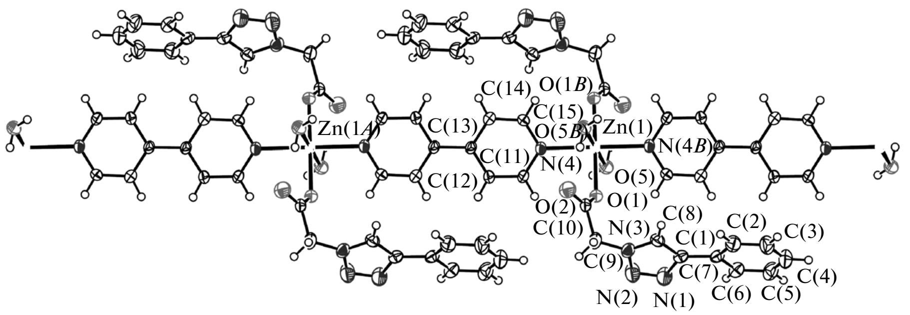

Fig. 1. The labeled ORTEP molecular structure of the compound shown as 30% thermal ellipsoid probability. Symmetry codes: (a) $x, y-1, z$; (b) $2-x, -y, 2-z$.

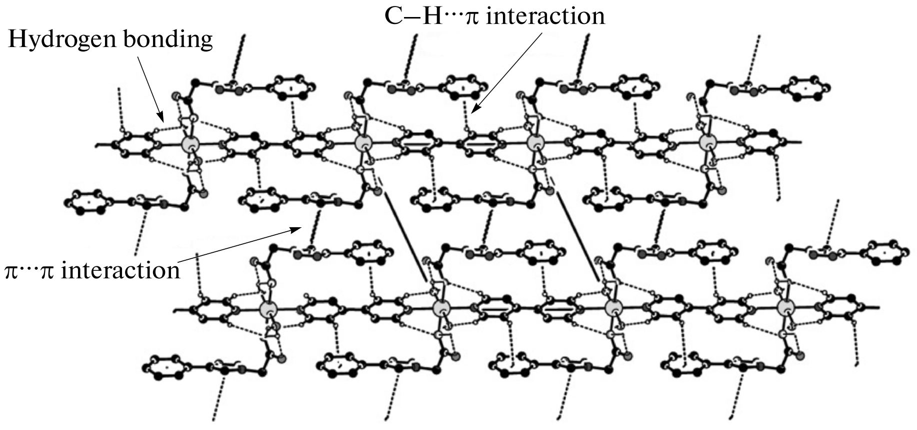

Fig. 2. The 3D structure of the complex and the interactions.

contains linear 1D chains formed by 4,4'-Bipy ligands connecting Zn atoms (Zn–Zn 11.514 Å). All Zn atoms are octahedrally [ZnO_4N_2] coordinated through four oxygen atoms from two Pta anions and two coordination water molecules (Zn–O 2.097(2) and 2.128(2) Å, respectively) and two nitrogen atoms from two 4,4'-Bipy ligands (Zn–N 2.201 Å). The Zn–N bond distances are similar to those found in related Zn(II)-4,4'-Bipy coordination polymers [15].

The abundant hydrogen bondings which plays an important role in forming 2D structure are observed in the layer: (a) H-bonding between the water and carboxylate O atom of thePta O(5)–H(5*B*)···O(1): O···H 2.16(5) Å, OHO 144(5)°; (b) H-bonding between the coordination water and another O atoms from the carboxylate O(5)–H(5*A*)···O(2): O···H 1.85(4) Å, OHO 175(8)°; (c) H-bonding between the C(6)–H(6) from benzene and N(1) atom of the triazole C(6)–H(6)···N(1): N···H 2.62 Å, CNO 100°; (d) H-bonding between the C(11)–H(11) of the pydine and O atom of the water C(11)–H(11)···O(5): O···H 2.57 Å, OHO 159°; (e) H-bonding between the C(15)–H(15) of the pydine and O atom of the Pta C(15)–H(15)···O(1): O···H 2.48 Å, OHO 118°, as shown in Table 3. In the 2D network, a C–H···π interaction was observed, i.e. C(12)–H(12)···*Cg* ($x, y-1, z$; *Cg* is the centroid of benzene C(1)–C(6) atoms) with the C···*Cg* distance of 3.696(6) Å. These adjacent 2D networks were further linked by a π···π interaction between two inversion-related triazole groups with the centroid-to-centroid distance of 3.652(3) Å, resulting in the final 3D network (Fig. 2).

The synthesized complex has been characterized by PXRD at room temperature. The peak positions of the simulated and experimental PXRD patterns are most agreement with each other, but the phase is not absolutely pure and it may be caused by impurity. The differences in reflection intensity may be due to the preferred orientation of the crystalline powder samples.

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I***

Bond	*d*, Å	Angle	ω, deg
Zn(1)–O(1)	2.097(3)	O(1)Zn(1)O(5)	88.46(13)
Zn(1)–O(5)	2.128(3)	O(5)Zn(1)N(4)	95.60(13)
Zn(1)–N(4)	2.201(4)	O(1)Zn(1)N(4)	87.62(13)

Table 3. Geometric parameters of hydrogen bonds for **I***

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(5)–H(5*A*)···O(2)^{i}	0.82(4)	1.85(4)	2.672(5)	175(8)
O(5)–H(5*B*)···O(1)^{ii}	0.80(5)	2.16(5)	2.850(5)	144(5)
C(6)–H(6)···N(1)	0.93	2.62	2.917(9)	100
C(11)–H(11*B*)···O(5)^{ii}	0.93	2.57	3.457(6)	159
C(15)–H(15)···O(1)^{i}	0.93	2.48	3.032(7)	118

* Symmetry codes: ^{i} $2 - x, -y, 2 - z$; ^{ii} $1 - x, -y, 2 - z$.

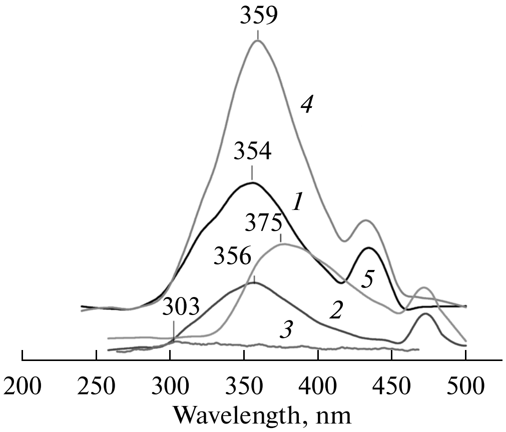

Fig. 3. The fluorescence spectra of HPta (*1*), 4,4'-Bipy (*2*), complex **I** (*3*), Pta with Zn(OAc)$_2$ (*4*), and 4,4'-Bipy with Zn(OAc)$_2$ (*5*).

Generally speaking, the complex with d^{10} configuration metal ions and aromatic organic are considered as solid photoluminescent materials [16]. Some 1,2,3-triazoles display special fluorescence properties, which can be used as fluorescent probe to test the metal ions in environment [17]. With the ligand and the complex in hand, the fluorescence properties were investigated, the corresponding emission spectra of the ligand and the complex in DMF at the room temperature are shown in Fig. 3. The maximum fluorescence emission of the Hpta and 4,4'-Bipy are 354 nm (λ_{ex} = 218 nm) and 356 nm (λ_{ex} = 238 nm), respectively. The blue-shift of the emission occurs to the complex (303 nm, λ_{ex} = 244 nm) due to the coordination with metal ion which change the rigidity of the ligand. There is an increasing of the intensity of the fluorescence when Zn(OAc)$_2$ was added into the ligand. However, the fluorescence quenching occurred for this complex, which probably be assigned to charge transfer due to the pta and 4,4'-bipy mutual coordination with Zn(II).

Thus, a new zinc(II) coordination polymer is designed by adopting 2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)acetic acid ligand and 4,4'-bipyridine. The polymer displays a three-dimensional layer structure, which is associated through metal coordination, hydrogen bonding and C–H···π together with π···π interactions. The fluorescent properties of the complex and ligand revealed that there was a co-effect of ancillary 4,4'-Bipy and HPta ligand for the quenching of fluorescence.

REFERENCES

1. Kolb, H.C., Finn, M.G., and Sharpless, K.B., *Angew. Chem. Int. Ed.*, 2001, vol. 40, p. 2004.
2. Agalave, S.G., Maujan, S.R., and Pore, V.S., *Chem. Asian J.*, 2011, vol. 6, p. 2696.
3. Ladmiral, V., Mantovani, G., Clarkson, G.J., et al., *J. Am. Chem. Soc.*, 2006, vol. 128, p. 4823.
4. Moses, J.E. and Moorhouse, A.D., *Chem. Soc. Rev.*, 2007, vol. 36, p. 1249.
5. Fu, Y., Li, H., Chen, X.-G., and Qin, J.-G., *Inorg. Chem. Commun.*, 2011, vol. 14, p. 268.
6. Simmons, J.T., Allen, J.R., Morris, D.R., et al., *Inorg. Chem.,* 2013, vol. 52, p. 5838.
7. Schweinfurth, D., Demeshko, S., Khusniyarov, M.M., et al., *Inorg. Chem.*, 2012, vol. 51, p. 7592.
8. Schweinfurth, D., Krzystek, J., Schapiro, I., et al., *Inorg. Chem.*, 2013, vol. 52, p. 6880.
9. Kilpin, K.J., Gavey, E.L., McAdam, C.J., et al., *Inorg. Chem.*, 2011, vol. 50, p. 6334.
10. Bratsos, I., Urankar, D., Zangrando, E., et al., *Dalton Trans.*, 2011, vol. 40, p. 5188.
11. Li, K.-H., Xu, K., Mei, S.-L., et al., *Chin. J. Inorg. Chem.*, 2013, vol. 29, p. 1312.
12. Shen, H.Y., Liao, D.Z., Jiang, Z.H., et al., *Polyhedron*, 1998, vol. 17, p. 1953.
13. Manisonial, A., Serafin, P., Traikia, M., et al., *Eur. J. Inorg. Chem.*, 2008, vol. 2008, p. 298.
14. Sheldrick, G.M., *SHELXL-97, Program for Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
15. Kim, J., Lee, U., and Koo, B.K., *Bull. Korean Chem. Soc.*, 2006, vol. 27, p. 918.
16. Allendorf, M.D., Bauer, C.A., Bhakta, R.K., and Houk, R.J.T., *Chem. Soc. Rev.*, 2009, vol. 38, p. 1330.
17. Hao, E.-H., Meng, T., Zhang, M., et al., *J. Phys. Chem. A*, 2011, vol. 115, p. 8234.