



## Hydrothermal Synthesis and Crystal Structure of (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>)

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(4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) (**1**) has been synthesized *via* hydrothermal reaction and characterized by single crystal X-ray diffraction. The crystal belongs to monoclinic, space group P2<sub>1</sub>/c with  $a = 7.7756(6)$ ,  $b = 21.536(2)$ ,  $c = 10.9188(8)$  Å,  $\beta = 106.606(1)^\circ$ ,  $C_{10}H_{10}N_2I_4Zn$ ,  $M_r = 731.17$ ,  $V = 1752.1(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.772$  g/cm<sup>3</sup>,  $S = 1.002$ ,  $\mu(\text{MoK}\alpha) = 8.433$  mm<sup>-1</sup>,  $F(000) = 1304$ ,  $R = 0.0239$  and  $wR = 0.0544$ . The crystal structure analysis of (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) shows that this compound features an isolated structure, based on discrete 4,4'-H<sub>2</sub>bipy moieties and tetrahedral zinc atoms terminally coordinated by four iodine atoms. The 4,4'-H<sub>2</sub>bipy and ZnI<sub>4</sub> moieties are interconnected by hydrogen bonds to yield a 1-D supramolecular chain.

**Key Words:** Bipyridine, Crystal structure, Halide, Hydrothermal, Zinc.

### INTRODUCTION

It is well-known that 4,4'-bipyridine (bipy) can act as a rod-like and rigid building block in the self-assembly of coordination frameworks, such as, acting as a charge-compensating cation<sup>1</sup>, an uncoordinated guest molecule and organic template<sup>2</sup>, a pillar bonding to inorganic skeletal backbone<sup>3</sup>, a bridge connecting two metal complex moieties<sup>4</sup> or a ligand linking a metal and an inorganic framework<sup>5</sup>. In recent years bipy has gained increased attention due to its common character-delocalized  $\pi$ -electrons of the pyridyl rings, which makes bipy an excellent candidate in preparing light emitting compounds whose potential in various technical applications, such as sensitizers in solar energy conversion<sup>6</sup>, chemical sensors<sup>7</sup> and emitting materials for organic light emitting diodes<sup>8</sup>. Nowadays, a lot of structures of metal halide-bipy materials have been reported<sup>9</sup>, however, among which, group 12 (IIB) metal halide-bipy materials are relatively rare. In fact, compounds containing IIB elements are particularly attractive for many reasons: the variety of coordination numbers and geometries provided by the  $d^{10}$  configuration of the IIB metal ions, the widespread applications of IIB compounds, fluorescent properties, photoelectric properties and the essential role in biological systems of zinc. Our recent efforts in synthesizing novel IIB-based compounds have focused largely on the systems containing bifunctional ligands, such as 4,4'-bipy. Herein we describe the synthesis and characterization of (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) (**1**).

### EXPERIMENTAL

**Synthesis of (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) (**1**):** All reactants of AR grade were obtained commercially and used without further purification. ZnI<sub>2</sub> (1 mmol, 319 mg), 4,4'-bipy (1 mmol, 156 mg), HI acid (1 mL) and distilled water (10 mL) were loaded into a Teflon-lined stainless steel autoclave (23 mL) and kept at 353 K for 10 days. After being slowly cooled to room temperature at a rate of 6 K/h, colourless crystals suitable for X-ray analysis were obtained. Yield: 62 % (based on zinc).

**X-Ray structure determination:** The intensity data set was collected on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by using a  $\omega$  scan technique. CrystalClear software was used for data reduction and empirical absorption corrections<sup>10</sup>. The structure was solved by the direct method using the Siemens SHELXTLTM Version 5 package of crystallographic software<sup>11</sup>. The difference Fourier maps based on the atomic positions yield all non-hydrogen atoms. The hydrogen atom positions were generated theoretically and allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters but was not refined. The structure was refined using a full-matrix least-squares refinement on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The selected bond lengths and bond angles are listed in Table-1. Temperature for data collection is 293(2) K. Reflections measured are 10383. Independent and observed reflections are 3039 and 2650,

TABLE-1

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)			
Bond	Dist.	Bond	Dist.
Zn(1)-I(1)	2.5979(6)	Zn(1)-I(3)	2.6266(6)
Zn(1)-I(2)	2.6369(6)	Zn(1)-I(4)	2.5931(6)
Angle	(°)	Angle	(°)
I(1)-Zn(1)-I(2)	106.25(2)	I(4)-Zn(1)-I(1)	110.13(2)
I(1)-Zn(1)-I(3)	109.64(2)	I(4)-Zn(1)-I(2)	109.76(2)
I(2)-Zn(1)-I(3)	111.04(2)	I(4)-Zn(1)-I(3)	109.95(2)

respectively, with  $R_{\text{int}} = 0.0241$ ,  $\theta_{\text{min}} = 2.71^\circ$ ,  $\theta_{\text{max}} = 25.02^\circ$ ,  $(\Delta\sigma)_{\text{max}} = 0.001$ ,  $(\Delta\rho)_{\text{max}} = 0.511$  and  $(\Delta\rho)_{\text{min}} = -0.939 \text{ e/Å}^3$ .

## RESULTS AND DISCUSSION

X-Ray diffraction analysis reveals that (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) is characterized by an isolated structure, consisting of 4,4'-H<sub>2</sub>bipy cations and tetraiodo-zinc anions, as shown in Fig. 1. The tetrahedral zinc atom is coordinated by four terminal iodine atoms with the bond lengths of Zn1-I1, Zn1-I2, Zn1-I3 and Zn1-I4 being of 2.5979(6), 2.6369(6), 2.6266(6) and 2.5931(6) Å (Table-2), respectively. The Zn-I distances are normal and comparable with those reported in the literature<sup>12</sup>. The bond angles of I-Zn-I are in the range of 106.25(2)-111.04(2)°, which are close to those in a regular tetrahedron. The charge of [ZnI<sub>4</sub>] moiety must be -2 due to the oxidation states of Zn and I are +2 and -1, respectively. For the requirement of charge balance, the nitrogen atoms of the 4,4'-H<sub>2</sub>bipy moieties must be protonated, as the cases found in many other compounds<sup>1</sup>. The two pyridyl rings of the 4,4'-H<sub>2</sub>bipy moieties are slightly twisted with a dihedral angle of 19.13°, which is comparable with that previously documented<sup>13</sup>. The 4,4'-H<sub>2</sub>bipy and [ZnI<sub>4</sub>] moieties are interconnected by C...I and N...I hydrogen bonds to give a 1-D supramolecular chain running along the a direction (Fig. 2). The hydrogen bonds and the electrostatic interactions between the (4,4'-H<sub>2</sub>bipy)<sup>2+</sup> cations and the [ZnI<sub>4</sub>]<sup>2-</sup> anions contribute to the stabilization of the crystal packing of the title compound (Fig. 3).

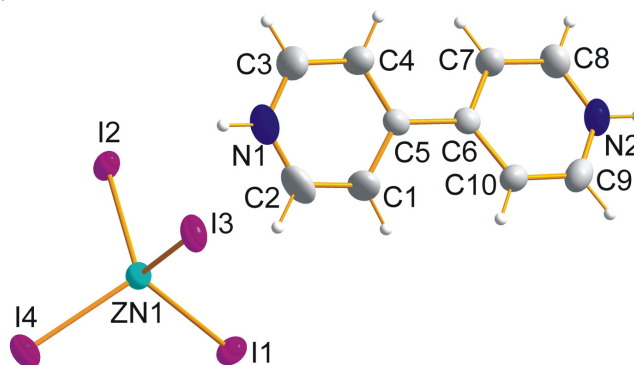


Fig. 1. ORTEP drawing of **1** with 30 % thermal ellipsoids. Hydrogen atoms were represented as small spheres

Generally, 4,4'-bipy molecule favours to link metal atoms into an extended structure, while discrete structures containing 4,4'-bipy ligands are relatively rare in IIB metal halides, to best of our knowledge, only one example has been reported<sup>14</sup>.

A search from the Cambridge Crystallographic Data Centre (CCDC) shows that there are over a dozen of compounds containing isolated [ZnI<sub>4</sub>]<sup>2-</sup> anions<sup>15</sup>. However, in these compounds the counterpart cations are various but none of them contains 4,4'-bipy moieties. Therefore, compound **1** is the first example of [ZnI<sub>4</sub>]<sup>2-</sup>-containing compounds with 4,4'-bipy moieties.

In brief, by using hydrothermal reactions of ZnI<sub>2</sub>, 4,4'-bipy and HI acid, a new compound was obtained. The crystal structure is characteristic of an isolated structure, based on discrete 4,4'-H<sub>2</sub>bipy moieties and tetrahedral zinc atoms terminally coordinated by four iodine atoms. A 1-D supramolecular chain is constructed from the 4,4'-H<sub>2</sub>bipy and the [ZnI<sub>4</sub>] moieties interconnecting *via* hydrogen bonds.

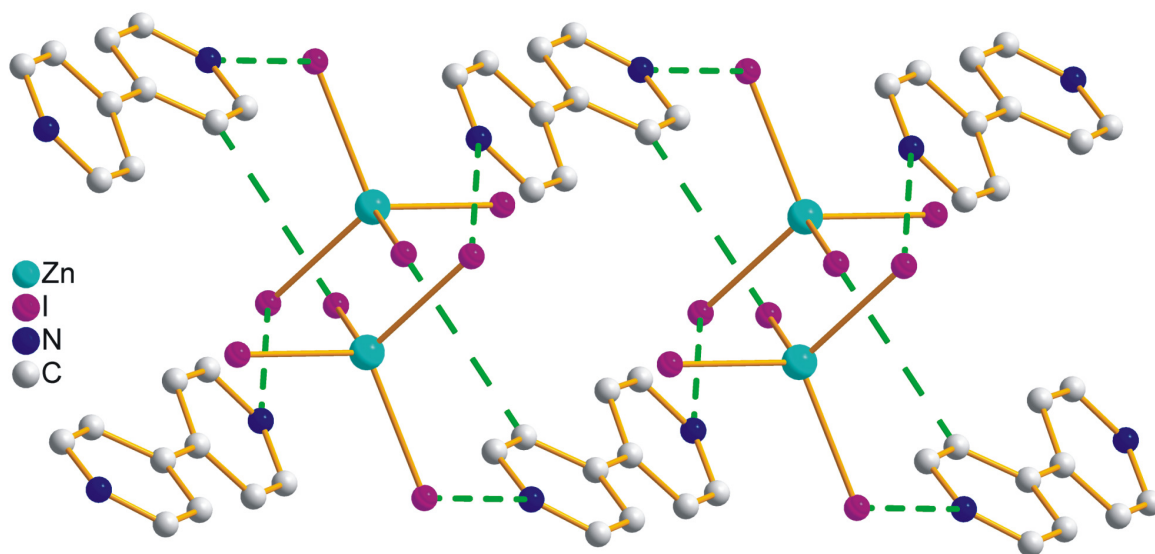
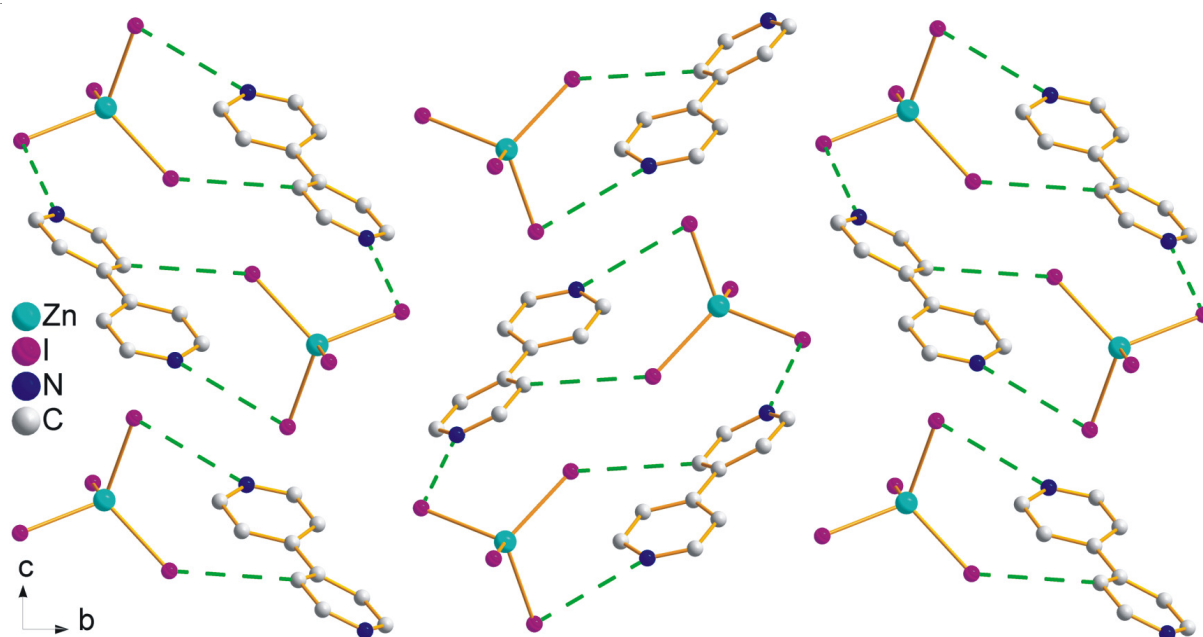


Fig. 2. 1-D supramolecular chain of **1** with the dashed lines representing hydrogen bonds. Hydrogen bond (Å): C(1)...I(1) 3.818(6), N(1)...I(2) 3.507(5) and N(2)...I(3) 3.703(4)

Fig. 3. Packing diagram of (4,4'-H<sub>2</sub>bipy)(ZnI<sub>4</sub>) (**1**)

## REFERENCES

1. Y. Lu, Y. Xu, E.B. Wang, J. Lü, C.W. Hu and L. Xu, *Cryst. Growth Des.*, **5**, 257 (2005).
2. K. Biradha and G. Mahata, *Cryst. Growth Des.*, **5**, 61 (2005).
3. (a) C.Y. Chen, K.H. Lii and A.J. Jacobson, *J. Solid State Chem.*, **172**, 252 (2003); (b) C.M. Wang, C.H. Wang, H.M. Kao and K.H. Lii, *Inorg. Chem.*, **44**, 6294 (2005).
4. (a) H. Jude, J.A.K. Bauer and W.B. Connick, *Inorg. Chem.*, **44**, 1211 (2005); (b) B.P. Yang and J.G. Mao, *Inorg. Chem.*, **44**, 566 (2005).
5. R.H. Wang, Y.F. Zhou, Y.Q. Sun, D.Q. Yuan, L. Han, B.Y. Lou, B.L. Wu, M.C. Hong, *Cryst. Growth Des.*, **5**, 251 (2005).
6. (a) A. Hagfeldt and M. Gratzel, *Acc. Chem. Res.*, **33**, 269 (2000); (b) V. Balzani and A. Juris, *Coord. Chem. Rev.*, **211**, 97 (2001).
7. S.S. Sun and A.J. Lees, *Organometallics*, **21**, 39 (2002).
8. F.G. Gao and A.J. Bard, *J. Am. Chem. Soc.*, **122**, 7426 (2000).
9. (a) B.N. Figgis, J.M. Patrick, P.A. Reynolds, B.W. Skelton, A.H. White and P.C. Healy, *Aust. J. Chem.*, **36**, 2043 (1983); (b) J. Lu, C. Yu, T.Y. Niu, T. Paliwala, G. Crisci, F. Somosa and A.J. Jacobson, *Inorg. Chem.*, **37**, 4637 (1998); (c) C.H. Hu, Q. Li and U. Englert, *Cryst. Eng. Commun.*, **5**, 519 (2003).
10. Rigaku, CrystalClear Version 1.35, Rigaku Corporation (2002).
11. Siemens, SHELXTLTM Version 5 Reference Manual, Siemens Energy & Automation Inc., Madison, Wisconsin, USA (1994).
12. (a) K. Hasebe, T. Asahi and K. Gesi, *Acta Crystallogr.*, **46C**, 218 (1990); (b) C.A. Grapperhaus, C.A. Mullins and M.S. Mashuta, *Inorg. Chim. Acta*, **358**, 623 (2005).
13. (a) N. Moliner, M.C. Munoz and J.A. Real, *Inorg. Chem. Commun.*, **2**, 25 (1999); (b) K. Al-Rasoul and T.J.R. Weakley, *Inorg. Chim. Acta*, **60**, 191 (1982).
14. (a) A.L. Gillon, A.G. Orpen, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín and C. Ruiz-Pérez, *Chem. Commun.*, 2287 (1999); (b) A.L. Gillon, G.R. Lewis, A.G. Orpen, S. Rotter, J. Starbuck, X.-M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez, *J. Chem. Soc. Dalton Trans.*, 3897 (2000).
15. W.T.A. Harrison, R.A. Howie, J. Skakle and J.L. Wardell, *Acta Crystallogr.*, **56C**, e124 (2000).