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**A NEW CRYSTALLINE FRAMEWORK FORMED FROM  
1,4-bis(4-PYRIDYLMETHYL)PIPERAZINE AND Cd(NO<sub>3</sub>)<sub>2</sub>:  
INTERPENETRATING MOLECULAR LADDERS FROM T-SHAPED BUILDING BLOCKS**

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Coordination of a pyridine-based bridging ligand, 4-bpmp, with cadmium nitrate afforded an infinite ladder-type complex  $\{[\text{Cd}(4\text{-bpmp})_2(\text{H}_2\text{O})\text{Cl}_2]\}_n$  (**A**) (4-bpmp = 1,4-bis(4-pyridylmethyl)piperazine) containing *T*-shaped building blocks. IR spectra, elemental analysis, and X-ray single-crystal diffraction were carried out to determine the composition and crystal structure of complex **A**. Inclined interpenetration of infinite ladders was observed in the solid structure. The combined work demonstrates the ability of bipyridyl coordination polymer leads to a novel metal complex with impressive structural motif.

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**Keywords:** 1,4-bis(4-pyridylmethyl)piperazine, *T*-shaped building blocks, metal complex.

### INTRODUCTION

The design and synthesis of functional polymers by means of the rational combination of bridging, bi- or multi-topic organic ligands with transition metal cations continues to attract enormous interest owing to their aesthetic ally appealing topologies and potential utility for gas storage, molecular separations, catalysis, ion exchange, molecular magnetism, luminescence, and so on [1–5]. It is widely acknowledged that the various framework structures can be controlled by careful-choosing the coordination geometry of metal ions and the chemical nature of organic ligands used in their formation [6, 7].

It has proved that the *T*-shape unit plays a significant role among numerous basic building blocks used in the construction of different architectures. In addition, it is known that the assembly of a  $\text{M}(\text{NO}_3)_2$  node with a bipyridyl ligand always leads to a *T*-shaped building block which will assemble into various network topologies and structural motifs including 1D ladders, 2D brick walls, parquet motifs, molecular bilayers, and 3D frameworks [8–11]. The bipyridyl ligands such as rigid 4,4'-bipyridine, non-right 1,2-bis(4-pyridyl)ethane, and several other analogous ligands are popular choice for the formation of *T*-shaped building units [12–14]. Employing of flexible bipyridyl ligands makes controlling of the eventual product more difficult, however, it provides more probability to achieve motifs with particular functions which are worth studying: (i) novel topological structures and framework entanglements (such as polycatenation and polythreading) [15]; (ii) variability of the networks (single or entangled) [16], and (iii) pleomorphism of conformation [17] that can result in a variety of chemical functions. Intriguingly, flexible bipyridyl ligands such as 1,4-bis(4-pyridylmethyl)piperazine (4-bpmp) [18, 19] have not been much explored in comparison with the great effort aimed at the progress of compounds containing rigid bipyridyl ligands.

In this paper, we report the synthesis and characterization of a new cadmium complex based on the flexible 4-bpmp ligand formulated as  $\{[\text{Cd}(\text{4-bpmp})_2 \cdot (\text{H}_2\text{O})\text{Cl}_2]\}_n$  (**A**). The *T*-shaped  $\text{Cd}(\text{4-bpmp})_3$  building blocks form infinite ladders, which interpenetrate each other in the crystal structure.

## EXPERIMENTAL

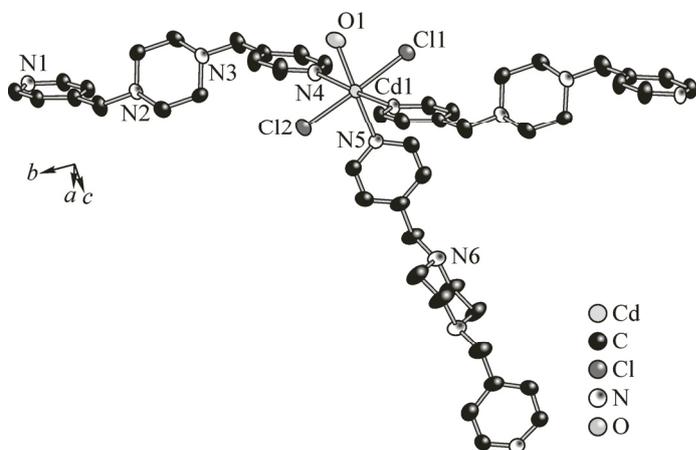
**Materials and physical measurements.** All chemicals and reagents were of reagent grade and used without further purification unless otherwise noted. Elemental analysis (C, H and N) was performed on a Finnigan EA 1112 analyzer. IR spectra were obtained in KBr disks on a Nicolet FT-IR 470 spectrometer in a range of 4000–400  $\text{cm}^{-1}$ .

**Synthesis of the complex.** In the experiment, the concentration of all reagents were 15 mM. Under stirring, 4-bpmp (10 mL) dissolved in ethanol solution was slowly added to an aqueous solution of  $\text{Cd}(\text{NO}_3)_2$  (10 mL). Then 0.2 M HCl solution was used to adjust the pH to 4. Stirring continued another 4 h. A transparent solution was obtained by filtration and left in an open beaker. Four days later, colorless block crystals were obtained at room temperature. The crystals were isolated after washing with distilled water and drying in air. Anal. Calcd. (%) for  $\text{C}_{32}\text{H}_{34}\text{CdCl}_2\text{N}_8\text{O}$ : C 44.90, H 6.59, N 17.46. Found (%): C 44.91, H 6.60, N 17.45. IR ( $\text{cm}^{-1}$ ): 2878 w, 1600 m, 1558 w, 1457 w, 1429 m, 1353 w, 1320 w, 1299 w, 1266 w, 1228 w, 1419 s, 1161 s, 1012 s, 1009 s, 842 s, 978 m, 940 m, 798 m, 642 m.

**X-ray crystal structure determination.** The crystal structure of the complex was determined by single-crystal X-ray diffraction. Data were collected on a Rigaku XtaLAB mini X-ray single crystal diffractometer with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.071073 \text{ \AA}$ ) at 566 K from  $3.02 < \theta < 27.51$ . The structure was solved by a direct method using the SHELXL-97 package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from different Fourier maps.

## RESULTS AND DISCUSSION

**Crystal structure of  $\{[\text{Cd}(\text{4-bpmp})_2(\text{H}_2\text{O})\text{Cl}_2]\}_n$  (**A**).** This complex exhibits a ladderlike structure where the Cd(II) centers are hexa-coordinated, as shown in Fig. 1. This hexa-coordinated  $\text{CdN}_3\text{OCl}_2$  environment is composed of one oxygen atom from a water molecule, two chloride ions and three nitrogen atoms from three independent 4-bpmp ligands bound to the metal ion in a distorted *T*-shaped geometry. The *T*-shaped framework of the molecular structure involves coordination angles somewhat divergent from the ideal values:  $\text{N4—Cd1—N5} = 92.8^\circ$ ,  $\text{N1—Cd1—N5} = 91.7^\circ$  and  $\text{N1—Cd1—N4} = 175.5^\circ$ . The self-assembled *T*-shaped  $\text{Cd}(\text{4-bpmp})_3$  building blocks give a 1D molecular ladder as shown in Fig. 2, with observably large  $\text{Cd}_4(\text{4-bpmp})_4$  rings with dimensions of  $17.01 \times 17.06 \text{ \AA}$  and angles of  $77.49^\circ$  and  $102.52^\circ$  (defined by  $\text{Cd} \cdots \text{Cd}$  distances and  $\text{Cd} \cdots \text{Cd} \cdots \text{Cd}$  angles). All 4-bpmp ligands take on the *Z*-conformation to constitute the rungs and side rails of the ladder, and this conformation is quite similar to that found in the first molecular ladder reported by Fujita [20] obtained from the reaction of  $\text{Cd}(\text{NO}_3)_2$  and 1,4-bis(4-pyridylmethyl)benzene (bpmb) in a 2:3



molar ratio. The independent ladders interpenetrate each other (Fig. 3). Each square window of the ladder interlocking four more rings of different ladders results in a 4-fold interpenetrated topology. Crystal data and structure refinement details are summarized in Table 1, selected bond lengths and angles are given in Table 2.

*Fig. 1.* Coordination environment of Cd1 with thermal ellipsoids at 50% probability and partial atom labeling. The 4-bpmp ligands are shown with complete skeleton. Hydrogen atoms have been omitted

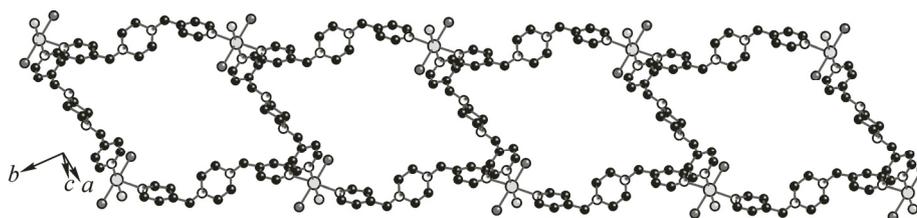


Fig. 2. The infinite ladder structure of the complex. Hydrogen atoms and the co-crystallized 4-bpmp molecules have been omitted

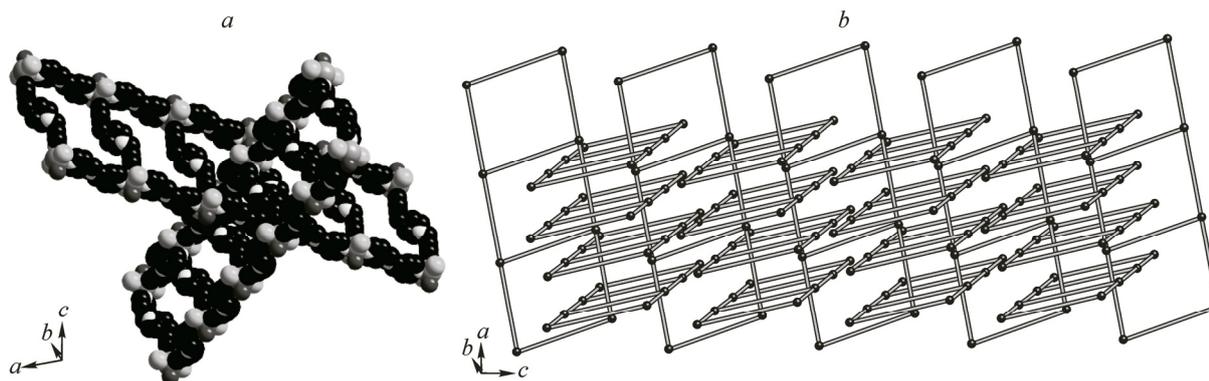


Fig. 3. Interpenetration in the crystal structure of the complex (a). Two interpenetrating ladders (b). Perspective view of the frameworks. Only the Cd(II) centers are shown; heavy connections indicate the Cd-1—Cd framework. Hydrogen atoms and the 4-bpmp molecules of crystallization have been omitted

Table 1

Crystal data and refinement for complex A

Parameter	Value
Empirical formula	$C_{32}H_{42}CdCl_2N_8O$
Formula weight, $g \cdot mol^{-1}$	738.03
Crystal system	Monoclinic
Space group	$P2(1)/n$
$a, b, c, \text{\AA}; \beta, \text{deg.}$	9.682(3), 13.987(5), 25.833(8); 94.384(4)
$V, \text{\AA}^3$	3488(2)
$Z$	4
Crystal size, mm	0.1×0.08×0.06
$F(000)$	1488
Calc. density, $g/cm^3$	1.390
$\theta$ range for data collection, deg.	$3.02 < \theta < 27.51$
Limiting indices	$-12 \leq h \leq 12, -18 \leq k \leq 17, -33 \leq l \leq 33$
Reflections collected	30088
Completeness, %	98.7
Goodness-of-fit on $F^2$	1.062
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0453, wR_2 = 0.1268$
$R$ indices, all data	$R_1 = 0.0487, wR_2 = 0.1295$
Largest diff. peak and hole, $e/\text{\AA}^3$	1.258 and $-0.601$

Selected bond lengths (Å) and angles (deg.) for complex A

Bond	<i>d</i>	Angle	$\omega$	Angle	$\omega$
Cd(1)—O(1)	2.361(3)	O(1)—Cd(1)—N(4) <sup>#1</sup>	87.20(11)	N(1)—Cd(1)—Cl(1)	89.41(7)
Cd(1)—N(4) <sup>#1</sup>	2.395(3)	O(1)—Cd(1)—N(1)	88.32(11)	N(5)—Cd(1)—Cl(1)	89.98(7)
Cd(1)—N(1)	2.402(3)	N(4) <sup>#1</sup> —Cd(1)—N(1)	175.48(9)	O(1)—Cd(1)—Cl(2)	88.73(7)
Cd(1)—N(5)	2.417(3)	O(1)—Cd(1)—N(5)	178.90(9)	N(4) <sup>#1</sup> —Cd(1)—Cl(2)	89.59(7)
Cd(1)—Cl(1)	2.5636(10)	N(4) <sup>#1</sup> —Cd(1)—N(5)	92.83(9)	N(1)—Cd(1)—Cl(2)	89.63(7)
Cd(1)—Cl(2)	2.5810(10)	N(1)—Cd(1)—N(5)	91.65(9)	N(5)—Cd(1)—Cl(2)	92.37(7)
N(4)—Cd(1) <sup>#4</sup>	2.395(3)	O(1)—Cd(1)—Cl(1)	88.93(7)	Cl(1)—Cd(1)—Cl(2)	177.49(3)
C(1)—N(1)	1.343(4)	N(4) <sup>#1</sup> —Cd(1)—Cl(1)	91.18(8)	C(5)—N(1)—C(1)	117.3(2)

## CONCLUSIONS

A Cd(II) complex containing 1,4-bis(4-pyridylmethyl)piperazine was synthesized and characterized by IR spectra, elemental analysis and X-ray diffraction. The complex has an infinite two-dimensional structure with interpenetrating molecular ladders. In light of this structural novelty observed with 4-bpmp, we are currently expanding our work on the *T*-shape unit system by experimenting with different bridging ligand systems in order to better elucidate the structure-directing effects of various ligands, and to gain a better understanding of the possibilities of crystal engineering.

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## REFERENCES

- Roswell J.L.C., Yaghi O.M. // *Angew. Chem., Int. Ed.* – 2005. – **44**, N 30. – P. 4670.
- Chen B., Liang C., Yang J. et al. // *Angew. Chem., Int. Ed.* – 2006. – **45**, N 2. – P. 1418.
- Han H., Zhang S., Hou H. et al. // *Eur. J. Inorg. Chem.* – 2006. – N 8. – P. 1594.
- Fang Q.-R., Zhu G.-S., Xue M. et al. // *Dalton Trans.* – 2006. – N 20. – P. 2399.
- Wu C.-D., Hu A., Zhang L. et al. // *J. Am. Chem. Soc.* – 2005. – **127**, N 25. – P. 8940.
- Gao E.-J., Wang K.-H., Gu X.-F. et al. // *J. Inorg. Biochem.* – 2007. – **101**, N 10. – P. 1404.
- Qi W., Cowan J.A. // *Coord. Chem. Rev.* – 2011. – **255**, N 7-8. – P. 688.
- Ciurtin D.M., Dong Y.-B., Smith M.D. et al. // *Inorg. Chem.* – 2001. – **40**, N 12. – P. 2825.
- Dong Y.-B., Layland R.C., Pschirer N.G. et al. // *Chem. Mater.* – 1999. – **11**, N 6. – P. 1413.
- Power N.K., Hennigar T.L., Zaworotko M.J. // *New J. Chem.* – 1998. – **22**, N 2. – P. 177.
- Yaghi O.M., Li H. // *J. Am. Chem. Soc.* – 1996. – **118**, N 1. – P. 295.
- Fujita M., Kwon Y.J., Sasaki O. et al. // *J. Am. Chem. Soc.* – 1995. – **117**. – P. 7287.
- Carlucci L., Ciani G., Maggini S. et al. // *Cryst. Growth Des.* – 2008. – **8**, N 1. – P. 162.
- Lu X.-Q., Jiang J.-J., zur Loye H.-C., Kang B.-S. // *Inorg. Chem.* – 2005. – **44**, N 6. – P. 1810.
- Carlucci L., Ciani G., Proserpio D.M. // *Coord. Chem. Rev.* – 2003. – **246**, N 1/2. – P. 247.
- Gao T., Wang X.-Z., Gu H.-X. et al. // *CrystEngComm.* – 2012. – **14**. – P. 5905.
- Leong W.L., Vittal J.J. // *Chem. Rev.* – 2011. – **111**, N 2. – P. 688.
- Martin D.P., Supkowski R.M., LaDuca R.L. // *Cryst. Growth Des.* – 2008. – **8**, N 10. – P. 3518.
- Farnum G.A., Wang C.Y., Gandolfo C.M. et al. // *J. Mol. Struct.* – 2011. – **998**, N 1-3. – P. 62.
- Fujita M., Sasaki O., Watanabe K. et al. // *New J. Chem.* – 1998. – **22**, N 2. – P. 189.