以 3,5-二(吡啶-4-甲氧基)苯甲酸为配体构筑的两个钡(II)、铅(II)配位聚合物

韩敏敏　　陈　晓　　张依萍　　冯云龙*

(浙江师范大学物理化学研究所,浙江省固体表面反应化学重点实验室,金华　321004)

摘要: 以 3,5-二(吡啶-4-甲氧基)苯甲酸(HL)为配体合成了 2 个配合物:[BaL$_2$]$_n$ (**1**)和[PbL(Ox)$_{0.5}$]$_n$ (**2**)(H$_2$(Ox)为草酸),并通过元素分析,红外光谱,热重和 X-射线单晶衍射实验对其结构进行了表征。分析表明,**1** 由 L-连接形成二维结构,通过苯环之间的 $\pi\cdots\pi$ 作用连接成三维网络结构;**2** 由于主配的连接形成二维层状结构,再通过辅配连接形成拓扑符号为(4^3)(4^4.5.6^{17}.7^2.8^2)(4.5^2)的三维网络结构。

关键词: 配合物;3,5-二(吡啶-4-甲氧基);$\pi\cdots\pi$ 作用;热重性质

Two Coordination Polymers Based on Bis(3,5-bis(pyrid-4-ylmethoxy)benzoic-acid) with Barium(II) and Plumbum(II)

HAN Min-Min　　CHEN Xiao　　ZHANG Yi-Ping　　FENG Yun-Long*

(*Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, College of Chemistry and Life Science, Zhejiang Normal University, Jinhua, Zhejiang 321004, China*)

Abstract: Two new coordination polymers [BaL$_2$]$_n$ (**1**) and [PbL(Ox)$_{0.5}$]$_n$ (**2**) (HL=3,5-bis(pyrid-4-ylmethoxy)benzoic acid, H$_2$(Ox)=Oxalic acid) have been synthesized under hydrothermal reaction and characterized by single crystal X-ray diffraction analysis. **1** displays a 2D framework and further enlarged its dimensionality to 3D net by $\pi\cdots\pi$ interactions between benzene rings with a centroid-centroid distance of 0.360 88(1) nm. **2** possesses a 3D (3,8)-connected net with the (4^3)(4^4.5.6^{17}.7^2.8^2)(4.5^2) topology. Thermogravimetric analyses (TGA) have been measured for both compounds. CCDC: 846216, **1**; 849062, **2**.

Key words: coordination polymers; 3,5-bis(pyrid-4-ylmethoxy)benzoic acid; $\pi\cdots\pi$ interactions; thermogravimetric property

0　Introduction

In recent years, design and research on metal-organic coordination polymers (MOCPs) have attracted more and more attentions in the fields of supramolecular chemistry due to the intriguing network topologies[1-10] and their potential applications such as cata-lysis, magnetism, luminescence and porosity, etc.[11-24]. As we all know, that aromatic polycarboxylic acids like 1,4-benzen-edicarboxylic acid, 1,3,5-benzene-tricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid are widely used to construct MOCPs[25-31]. 3,5-Bis (pyrid-4-ylmethoxy)benzoic acid (HL) is one kind of suitable building linker since it is a polytopic ligand

with long bridges between the donor atoms which can provide more coordination sites for metal centers. The long-exible ligand may be a good candidate as an unique structural motif to produce architectures with interesting topologies and useful functional properties[32]. With this aim of understanding the coordination chemistry of HL[33-39] and preparing new materials with excellent physical properties, we choose 3,5-bis(pyrid-4-ylmethoxy)benzoic acid as our ligand and have already synthetized these kinds of polymer compounds with such ligands[40-41].

Aromatic-aromatic or $\pi \cdots \pi$ interactions are important non-covalent intermolecular forces similar to hydrogen bonding. They can contribute to self-assembly or molecular recognition processes when extended structures are formed from building blocks with aromatic moieties[42-43]. In the area of metal-ligand compounds, the importance of information gained from crystal structures on the covalent metal-ligand bond distances and angles has often over-shadowed the additional information available from $\pi \cdots \pi$ interactions: how the complexes or coordination polymers are packed in their crystal lattice[44-45]. 3,5-Bis(pyrid-4-ylmethoxy) benzoic acid is just one kind of suitable building block with aromatic-aromatic or $\pi \cdots \pi$ interactions.

Herein, we report the synthesis and structure of two coordination polymers constructed from HL ligand.

1 Experimental

1.1 Materials and general methods

All solvents and starting materials for the synthesis were purchased commercially without further purification. Compounds were obtained under hydrothermal reaction in a 25 mL Teflon lined stainless steel Parr bomb. The diffraction data collection was performed with Mo $K\alpha$ radiation ($\lambda = 0.071\ 073$ nm) on a Bruker APEX Ⅱ area-detector diffractometer. Elemental analyses were carried out using a Perkin-Elmer 2400 Ⅱ elemental analyzer. Thermogravimetric analysis (TG) was performed at a rate of 10 ℃·min^{-1} under oxygen stream using a Netzsch STA449C apparatus. IR spectrum was measured in KBr pellets on a Nicolet 5DX FTIR

spectrometer.

1.2 Synthesis of the Polymers

1.2.1 Synthesis of [BaL$_2$]$_n$ (**1**)

A mixture of HL (0.0506 g, 0.15 mmol), Ba(NO$_3$)$_2$ (0.039 2 g 0.15 mmol) and NaOH (0.006 g, 0.15 mmol) were dissolved in purified water (15 mL) in a 25 mL stainless steel reactor with a telflon liner and heated at 433 K for 72 h, and then cooled to room temperature at a speed of 5 ℃·h^{-1}. Yellow single crystals of **1** were obtained by slow evaporation of the filtrate over a few days. Anal. Calcd.(%) for C$_{38}$H$_{30}$N$_4$O$_8$Ba (808.01): C, 56.49; H, 3.74; N, 6.93. Found (%): C, 56.43; H, 3.74; N, 6.93. IR (KBr, cm^{-1}): 3 443, 3 018, 1 621, 1 541, 1 373, 1 178, 1 065, 880, 769, 690.

1.2.1 Synthesis of [PbL(Ox)$_{0.5}$]$_n$ (**2**)

A mixture of HL (0.050 6 g, 0.15 mmol), Pb(Ac)$_2$ (0.048 8 g, 0.15 mmol), Oxalic acid (0.018 9 g, 0.15 mmol) and NaOH (0.006 g, 0.15 mmol) were dissolved in purified water (15 mL) in a 25 mL stainless steel reactor with a telflon liner and heated at 433 K for 72 h, and then cooled to room temperature at a speed of 5 ℃·h^{-1}. Yellow single crystals of **2** were obtained by slow evaporation of the filtrate over a few days. Anal. Calcd.(%) for C$_{20}$H$_{15}$N$_2$O$_6$Pb (586.55): C, 40.95; H, 2.58; N, 4.78. Found (%): C, 40.57; H, 2.59; N, 4.78. IR (KBr, cm^{-1}): 3 431, 2 996, 1 627, 1 586, 1 458, 1 243, 1 165, 1 068, 897, 785, 720.

1.3 Single-crystal structure determination

The diffraction data for the polymers **1** and **2** were collected on a Bruker SMART APEX Ⅱ CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071\ 073$ nm) at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structure was solved with direct methods and expanded with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically. All calculations were performed using SHELXS-97[46] and SHELXL-97[47] program packages. Further details for structural analyses are summarized in Table 1, selected bond lengths and angles are listed in Table 2.

CCDC: 846216, **1**; 849062, **2**.

Table 1　Crystal data and structure refinements for the 1 and 2

	1	2
Empirical formula	$C_{38}H_{30}BaN_4O_8$	$C_{20}H_{15}N_2O_6Pb$
Formula weight	808.00	586.54
Color	Yellow	Yellow
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a / nm	1.308 23(2)	0.986 14(10)
b / nm	1.039 88(2)	1.010 55(11)
c / nm	2.442 04(4)	1.129 04(12)
α / (°)		65.250(6)
β / (°)	98.256 0(10)	84.059(7)
γ / (°)		66.936(6)
V / nm³	3.287 73(10)	0.937 64(17)
Z	4	2
D_c / (g·cm⁻³)	1.632	2.077
μ / mm⁻¹	1.271	9.038
$F(000)$	1 624	558
$\theta_{min}, \theta_{max}$ / (°)	1.67, 27.57	1.99, 27.55
Reflections collected	50 466	14 980
Unique reflections (R_{int})	7 586(0.047 6)	4 291(0.032 4)
Observed reflections ($I>2\sigma(I)$)	5 659	4 291
Parameters refined	460	262
Goodness-of-fit (F^2)	1.02	1.021
R, wR ($I>2\sigma(I)$)	0.049 1, 0.144 4	0.024 6, 0.050 9
R, wR (all data)	0.068 8, 0.159 0	0.030 8, 0.052 8
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ / (e·nm⁻³)	745, −678	919, −790

Table 2　Selected bond lengths (nm) and angles (°) for the complex 1 and 2

1					
Ba(1)-O(1)	0.226 9(3)	Ba(1)-O(5)	0.301 0(4)	Ba(1)-N(1)#3	0.242 8(4)
Ba(1)-O(2)	0.258 1(4)	Ba(1)-N(2)#1	0.232 8(4)		
Ba(1)-O(6)	0.221 5(3)	Ba(1)-N(4)#2	0.237 8(4)		
O(6)-Ba(1)-N(1)#3	88.17(14)	O(6)-Ba(1)-N(2)#1	128.69(14)	O(1)-Ba(1)-N(1)#3	89.72(14)
O(1)-Ba(1)-N(2)#1	141.75(12)	N(2)#1-Ba(1)-N(1)#3	90.18(14)	O(6)-Ba(1)-N(4)#2	92.16(13)
N(4)#2-Ba(1)-N(1)#3	178.39(13)	O(1)-Ba(1)-N(4)#2	91.86(13)	O(6)-Ba(1)-O(2)	143.04(12)
N(2)#1-Ba(1)-N(4)#2	88.38(13)	O(1)-Ba(1)-O(2)	53.78(10)	N(2)#1-Ba(1)-O(2)	88.01(11)
N(1)#3-Ba(1)-O(2)	87.49(13)	N(4)#2-Ba(1)-O(2)	93.18(12)	O(6)-Ba(1)-O(1)	89.53(13)
O(6)-Ba(1)-O(5)	46.88(12)	O(1)-Ba(1)-O(5)	134.96(10)	N(2)#1-Ba(1)-O(5)	82.81(11)
N(4)#2-Ba(1)-O(5)	81.01(12)	N(1)#3-Ba(1)-O(5)	98.09(13)	O(2)-Ba(1)-O(5)	169.25(10)
2					
Pb(1)-O(2)	0.236 8(3)	Pb(1)-N(2)#3	0.291 3(4)	Pb(1)-O(1)#4	0.295 9(3)
Pb(1)-O(5)#1	0.246 2(3)	Pb(1)-O(1)	0.262 3(3)		
Pb(1)-O(6)	0.247 0(3)	Pb(1)-N(1)#2	0.270 3(3)		
O(2)-Pb(1)-O(5)#1	84.13(10)	O(6)-Pb(1)-O(1)	73.39(9)	O(2)-Pb(1)-O(6)	78.88(10)

Continued Table 2

O(2)-Pb(1)-N(1)#2	78.54(10)	O(5)#1-Pb(1)-O(6)	66.66(9)	O(5)#1-Pb(1)-N(1)#2	74.92(10)
O(2)-Pb(1)-O(1)	52.16(8)	O(6)-Pb(1)-N(1)#2	136.93(10)	O(5)#1-Pb(1)-O(1)	125.42(9)
O(1)-Pb(1)-N(1)#2	117.77(10)	O(2)-Pb(1)-N(2)#3	136.40(12)	O(5)#1-Pb(1)-N(2)#3	114.95(12)
O(6)-Pb(1)-N(2)#3	74.56(11)	O(1)-Pb(1)-N(2)#3	87.02(12)	N(1)#2-Pb(1)-N(2)#3	142.45(12)
O(2)-Pb(1)-O(1)#4	85.40(9)	O(5)#1-Pb(1)-O(1)#4	153.98(9)	O(6)-Pb(1)-O(1)#4	133.98(8)
O(1)-Pb(1)-O(1)#4	62.97(10)	N(1)#2-Pb(1)-O(1)#4	79.69(9)	N(2)#3-Pb(1)-O(1)#4	88.80(10)

Symmetry transformations used to generate equivalent atoms: **1**: #1 $x+1/2$, $-y+1/2$, $z+1/2$; #2 x, $y-1$, z; #3 x, $y+1$, z; #4 $x-1/2$, $-y+1/2$, $z-1/2$; **2**: #1 $-x$, $-y$, $-z+1$; #2 $x+1$, $y-1$, $z+1$; #3 $x-1$, y, $z+1$; #4 $-x$, $-y+1$, $-z+1$; #5 $x-1$, $y+1$, $z-1$; #6 $x+1$, y, $z-1$.

2 Results and discussion

2.1 Crystal structure of [BaL₂]ₙ (1)

1 crystallizes in the monoclinic space group $P2_1/n$ with an asymmetric unit consisting of one Ba(II) ion and two L⁻ ligands, as shown in Fig.1a. The Ba1 is seven-coordinated by three nitrogen atoms (Ba-N 0.232 8(4)~0.242 8(4) nm) and four oxygen atoms (Ba-O 0.226 9(3)~0.301 0(4) nm) from five L⁻ ligands to form a distorted pentagonal bipyramid geometry.

The carboxylate group of the L⁻ ligand is deprotonated and coordinates to a Ba(II) ion in bidentate mode. The carboxylate groups and N atoms of two L⁻ ligands bridge the Ba(II) ions into one 1D double chain, then the neighboring chains are further interconnected by another N atom from one of the L⁻ ligands to generate the 2D layers (Fig.1b).

It is well-known that $\pi\cdots\pi$ interactions are necessary in the formation and stability of supermolecular structures. As expected, the parallel benzene rings between adjacent layers exist strong $\pi\cdots\pi$ interactions with a centroid-centroid distance of 0.360 88(1) nm to form a 3D framework (Fig.1c).
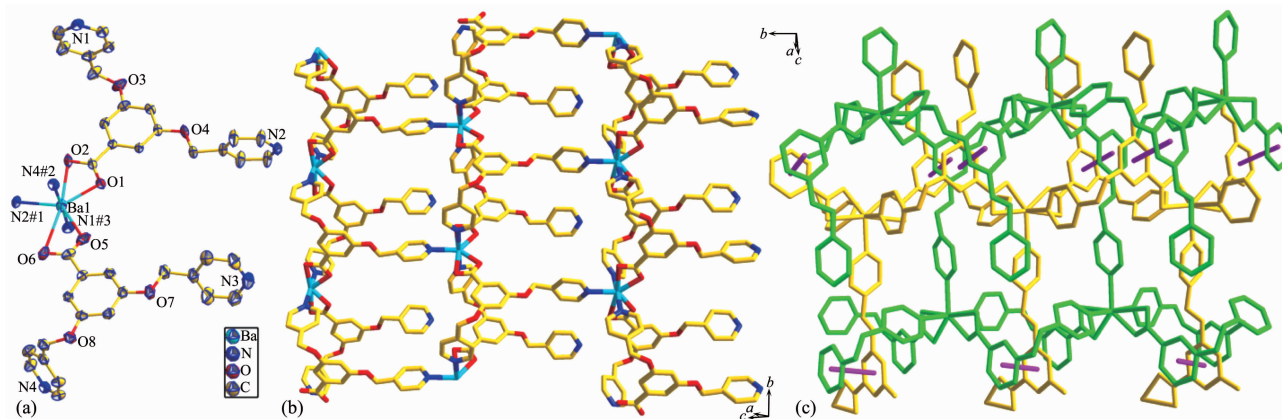
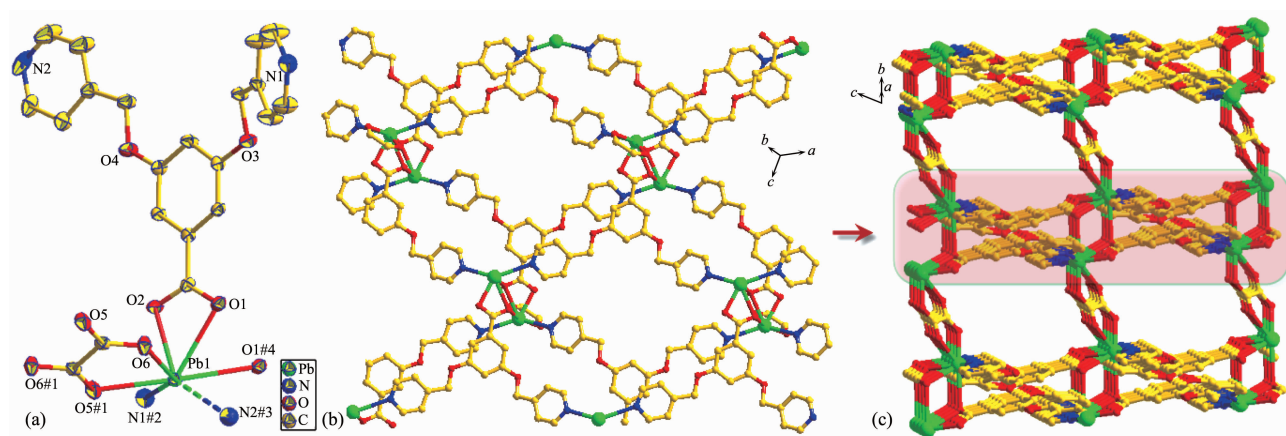Thermal ellipsoids are shown at the 50% probability level; H atoms are omitted for clarity;
Symmetry codes: #1 $x+1/2$, $-y+1/2$, $z+1/2$; #2 x, $y-1$, z; #3: x, $y+1$, z

Fig.1 (a) Coordination environment of the Ba(II) ions in **1** showing the atom labeling, (b) View of 2D framework,
(c) $\pi\cdots\pi$ interactions between the parallel benzene rings

2.2 Crystal structure of [PbL(Ox)₀.₅]ₙ (2)

2 crystallizes in the triclinic space group $P\bar{1}$ consisting of one Pb(II) ion, one L⁻ ligand and half one of Ox²⁻ ligand (Fig.2a). The Pb(1) is six-coordinated by one nitrogen atom (Pb-N 0.270 3(3) nm) from L⁻ ligands, three oxygen atoms (Pb-O 0.236 8(3)~0.262 3(3) nm) from two L⁻ ligands and two oxygen atoms (Pb-O 0.246 2(3)~0.247 0(3) nm) from Ox²⁻ ligands. The Pb-O and Pb-N bond lengths are all in the normal ranges. It is worth noting that the distance between Pb(1) and N(2)#3 is 0.291 3(4) nm which indicates weak interaction between them. If considering this interaction as a weak dentative bond, the Pb(1) is seven-coordinated by two nitrogen atoms and five oxygen atoms to form a distorted pentagonal bipyramid geometry.

Thermal ellipsoids are shown at the 35% probability level; H atoms are omitted for clarity; Symmetry codes:
#1 $-x$, $-y$, $-z+1$; #2 $x+1$, $y-1$, $z+1$; #4 $-x$, $-y+1$, $-z+1$; #5 $x-1$, $y+1$, $z-1$; #6 $x+1$, y, $z-1$

Fig.2　(a) Coordination environment of the Pb(Ⅱ) ions in **2** showing the atom labeling, (b) View of 2D layers generated by L$^-$ ligands and Pb(Ⅱ) ion, (c) View of 3D framework of compound **2**
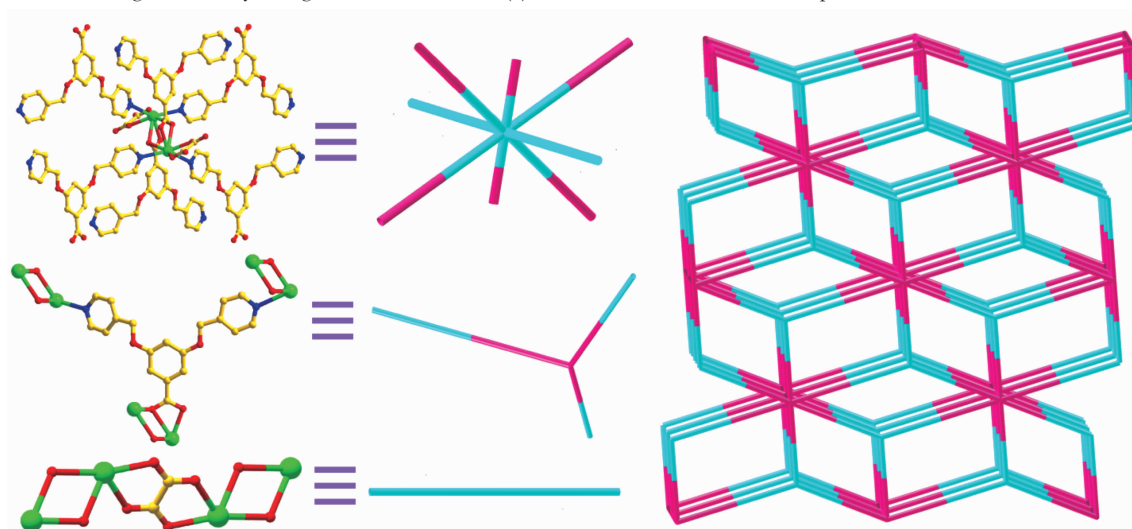

Fig.3　Schematic representation of the (3,8)-connected framework with $(4^3)(4^4.5.6^{17}.7^2.8^2)(4.5^2)$ topology of **2**

The carboxylate group of the L$^-$ ligand is deprotonated and coordinate to the Pb(Ⅱ) ion in bidentate mode. The L$^-$ ligands connectde Pb(Ⅱ) ions by carboxylate oxygen atoms and nitrogen atoms into 2D layer (Fig. 2b) and then connected by one Ox^{2-} ligand to form 3D framework (Fig.2c). The strong $\pi\cdots\pi$ interactions between parallel benzene rings stabilized the 3D network .

As shown in Fig.3, the two Pb(Ⅱ) ions form a binuclear unit through bondings from carboxylate groups of L$^-$ ligands. Each binuclear unit attached to six L$^-$ ligands and two Ox^{2-} ligands to represent a 8-connected node; each L$^-$ ligand connect three binuclear units to present a 3-connected node and each Ox^{2-}

ligand can be seen as a linear linker between two binuclear units. Complex **2** possesses a 3D (3,8)-connected net with the $(4^3)(4^4.5.6^{17}.7^2.8^2)(4.5^2)$ topology.

2.3　Thermal analyses

Thermogravimetric analyses (TGA) have been measured for all compounds (Fig.4). For **1**, the network remained intact until it was heated to 365 ℃ implying higher thermal stability of the frameworks and then began to collapse. The total observed weight loss at 483 ℃ is 82.16% and the final residuals may be BaO (Calcd. 81.02%). The oxalic acids were gradually lost in the temperature range 193~248 ℃ for **2** (Obsd. 8.63%, Calcd. 7.50%). Above this temperature, the weight loss is due to the decomposition of

the organic ligands and the collapse of the whole framework and the final residuals may be PbO (Obsd. 56.23%, Calcd. 52.74%).
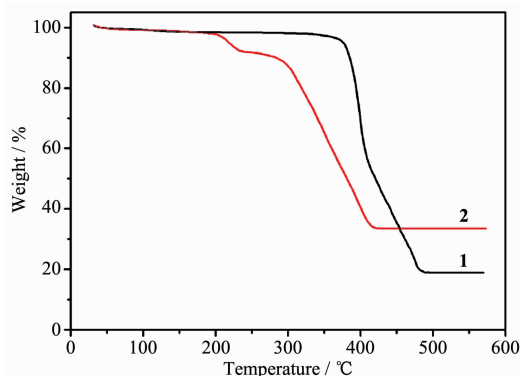

Fig.4　Thermogravimetric curves for **1** and **2**

3　Conclusions

In summary, we have successfully synthesized two new MOCPs based on bis (3,5-bis (pyrid-4-ylmehoxy)benzoic acid under hydrothermal conditions. **1** crystallizes in the $P2_1/n$ space group and shows a 2D framework which stabilized by $\pi\cdots\pi$ interactions between benzene rings with a centroid-centroid distance of 0.360 88(1) nm. **2** crystallizes in the $P\bar{1}$ space group and shows a 3D (3,8)-connected net with the $(4^3)(4^4.5.6^{17}.7^2.8^2)(4.5^2)$ topology.

References:

[1] Hao Z M, Zhang X M. *Cryst. Growth Des.*, **2008**,**8**:3586-3590

[2] Chen J, Feng Y L, Jiang Z G, et al. *CrystEngComm*, **2011**, **13**:6071-6075

[3] Kirillov A M. *Coord. Chem. Rev.*, **2011**,**255**:1603-1607

[4] Wang S, Ding X H, Zuo J L, et al. *Coord. Chem. Rev.*, **2011**,**255**:1713-1717

[5] Sumby C J. *Coord. Chem. Rev.*, **2011**,**255**:1937-1941

[6] Kennedy S, Dodgson I E, Beavers C M, et al. *Cryst. Growth Des.*, **2012**,**12**:688-671

[7] Cholewa P P, Beavers C M, Teat S J, et al. *Cryst. Growth Des.*, **2013**,**13**:2703-2706

[8] Kong G Q, Wu C D. *Cryst. Growth Des.*, **2010**,**10**:4590-4595

[9] Stock N, Biswas S. *Chem. Rev.*, **2012**,**112**:933-969

[10]Yu F, Zhang S J, Zhao X, et al. *Cryst. Growth Des.*, **2010**, **10**:1871-1875

[11]Peasw A R, Jeppesen J O, Luo Y, et al. *Acc. Chem. Res.*, **2001**,**34**:433-437

[12]Bradshaw D, Claridge J B, Cussen E J, et al. *Acc. Chem. Res.*, **2005**,**38**:273-277

[13]Li J R, Sculley J, Zhou H C, et al. *Chem. Rev.*, **2012**,**112**: 869-932

[14]Song J F, Chen Y, Li Z G, et al. *J. Mol. Struct.*, **2007**,**842**: 125-129

[15]He Y H, Lan Y Z, Zhan C H, et al. *Inorg. Chim. Acta*, **2009**,**362**:1952-1955

[16]Zhao S N, Su S Q, Song X Z, et al. *Cryst. Growth Des.*, **2013**,**13**:2756-2765

[17]Choi H J, Suh M P. *J. Am. Chem. Soc.*, **1998**,**120**:10622-10627

[18]Eslava S, Papageorgiou A C, Beaumont S K, et al. *Chem. Mater.*, **2010**,**22**:5175-5175

[19]Noro S, Kitagawa S, Kondo M, et al. *Angew. Chem. Int. Ed.*, **2000**,**39**:2082-2086

[20]Zhang J, Li Z J, Kang Y, et al. *Inorg. Chem.*, **2004**,**43**:8085-8089

[21]Cametti M, Nissinen M, Cort A D, et al. *J. Am. Chem. Soc.*, **2005**,**127**:3831-3835

[22]Ma Z, Moulton B. *Coord. Chem. Rev.*, **2011**,**255**:1623-1627

[23]Liu C B, Yu M X, Zheng X J, et al. *Inorg. Chim. Acta*, **2005**,**358**:2687-2690

[24]Liu J, Thallapally P K, Mcgral B P, et al. *J. Chem. Soc.*, **2012**,**41**:2308-2322

[25]Hu B W, Zhao J P, Sanudo E C, et al. *Dalton Trans.*, **2008**: 5556-5560

[26]Duan Z, Zhang Y, Zhang B, et al. *J. Am. Chem. Soc.*, **2009**, **131**:6934-6937

[27]Prasad T K, Rajasekharan M V, Costes J P. *Angew. Chem. Int. Ed.*, **2007**,**46**:2851-2857

[28]Pachfule P, Das R, Poddar P, et al. *Cryst. Growth Des.*, **2010**,**10**:2475-2478

[29]Wang X J, Huang T H, Tang L H, et al. *CrystEngCommun*, **2010**,**12**:4356-4364

[31]Li H, Zhao B, Ding R, et al. *Cryst. Growth Des.*, **2012**,**12**: 4170-4179

[31]Zhang H, Lu Y, Zhang Z, et al. *Chem. Commun.*, **2012**,**48**: 7295-7297

[32]Xu G J, Zhao Y H, Shao K Z, et al. *J. Mol. Struct.*, **2010**, **983**:93-97

[33]Xu G J, Zhao Y H, Shao K Z, et al. *CrystEngComm*, **2009**, **11**:1842-1846

[34]Xu G J, Zhao Y H, Shao K Z, et al. *Polyhedron*, **2009**,**28**:

3155-3159

[35]Xu G J, Zhao Y H, Shao K Z, et al. *Z. Anorg. Allg. Chem.*, **2009,635**:2671-2675

[36]Xu G J, Zhao Y H, Shao K Z, et al. *Inorg. Chem. Commun.*, **2010,13**:932-936

[37]Xu G J, Zhao Y H, Shao K Z, et al. *Inorg. Chem. Commun.*, **2009,12**:1024-1027

[38]Xu G J, Zhao Y H, Shao K Z, et al. *Inorg. Chem. Commun.*, **2009,12**:969-973

[39]Ashiry K O, Zhao Y H, Shao K Z, et al. *Inorg. Chem. Commun.*, **2008,11**:1181-1185

[40]ZHANG Yi-Ping(张依萍), CHEN Jing(陈静), CAI Yan-Ni (蔡艳妮), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2012,31**:1441-1445

[41]Hong L, Zhang Y P. *Acta Crystallogr.*, **2012,E69**:077-080

[42]Amabilino D B, Stoddart J F. *Chem. Rev.*, **1995,95**:2725-2729

[43]Hirsch K A, Wilson S R, Moore J S. *Chem. Eur. J.*, **1997,3**:765-769

[44]Guckian K M, Schweitzer B A, Ren R X F, et al. *J. Am. Chem. Soc.*, **2000,122**:2213-2217

[45]Janiak C. *Dalton Trans.*, **2000**:3885-3889

[46]Sheldrick G M. *SHELXS* 97, *Program for the Solution of Crystal Structures*, Germany, University of Göttingen, **1997**.

[47]Sheldrick G M. *SHELXTL* 97, *Program for the Refinement of Crystal Structures*, Germany, University of Göttingen, **1997**.