

酰胺氮桥联双核钴(III)配合物 $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ 的合成、分子结构和超分子组装

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摘要: 合成了 1 个酰胺氮桥联的双核钴(III)配合物 $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ ($\text{bpmb}^{2-}=1,2\text{-bis}(\text{pyridine-2-carboxamido})\text{-4-methylbenzenate}$) (**1**), 并通过 X-射线单晶衍射分析表征其结构特征。结果表明: 吡啶甲酰胺配体 H_2bpmb 的甲酰胺氮原子脱去氢原子形成带两个负电荷的扭曲的四配位螯合配体 bpmb^{2-} 。1 个钴(III)离子与 2 个吡啶氮原子, 2 个 bpmb^{2-} 配体上的桥联酰胺氮原子和 2 个氰基碳原子配位得到六配位、变形的八面体 CoN_4C_2 ; 另 1 个钴(III)离子与 2 个吡啶氮原子, 配体 bpmb^{2-} 上的 2 个未桥联甲酰胺氮原子和 2 个桥联的甲酰胺氮原子六配位, 形成扭曲的八面体 CoN_6 配位构型。 $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2]$ 单元通过自由水分子和氰基氮原子和甲酰胺氧原子之间 $\text{O-H}\cdots\text{N}$ 和 $\text{O-H}\cdots\text{O}$ 氢键形成锯齿型链状超分子亚结构, 这些链状亚结构通过 $\pi\text{-}\pi$ 相互作用连接起来形成网状的超分子结构。

关键词: 钴(III)配合物; 晶体结构; 超分子组装; 酰胺氮桥联

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Synthesis, Molecular Structure and Supramolecular Assembly of a Carboxamide Nitrogen-Bridged Dicobalt(III) Complex $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ ($\text{bpmb}^{2-}=1,2\text{-bis}(\text{pyridine-2-carboxamido})\text{-4-methylbenzenate}$)

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Abstract: A carboxamide nitrogen-bridged binuclear cobalt(III) complex $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ ($\text{bpmb}^{2-}=1,2\text{-bis}(\text{pyridine-2-carboxamido})\text{-4-methylbenzenate}$) (**1**) has been synthesized and structurally characterized by single X-ray diffraction analysis. In the molecular structure, the pyridine carboxamide ligand H_2bpmb forms twisted tetradentate chelate ligand bpmb^{2-} with two negative charges after the deprotonation of the two carboxamide nitrogen atoms. One Co(III) ion is coordinated by two pyridine nitrogen, two bridging carboxamide nitrogen atoms from two bpmb^{2-} ligands, and two *cis*-cyanide carbon atoms, giving distorted octahedral CoN_4C_2 environment. Another Co(III) ion in **1** is six-coordinated by two pyridine nitrogen, two unbridging carboxamide nitrogen and two bridging carboxamide nitrogen atoms from two bpmb^{2-} ligands, yielding significantly distorted octahedral CoN_6 geometry. It is noteworthy that the $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2]$ units are connected through two $\text{O-H}\cdots\text{N}$ and $\text{O-H}\cdots\text{O}$ hydrogen bonds involving free water molecules and cyanide nitrogen and carboxamide oxygen atoms into zigzag chain-like substructures, then these chains are linked together by intermolecular $\pi\text{-}\pi$ interactions, giving a network supramolecular structure. CCDC: 661715.

Key words: cobalt(III) complex; crystal structure; supramolecular assembly; carboxamide nitrogen-bridged

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0 Introduction

In the past three decades, the design, synthesis, crystal structures and properties of metal-organic complexes bridged by various groups such as hydroxo, methoxo, oxalato, chloro, cyano and azido have attracted much attention in the field of chemistry, physics and material as well as biology with the aim of developing new functional materials and elucidating the correlation between structures and properties^[1-6]. Among these research processes, the peripheral ligands around the center metal ions always play very important roles because of not only their dentate number, steric structure, rigidity and flexibility, and charge number but also the bridging roles of coordinated atoms from these peripheral ligands. Therefore, the design and selection of suitable organic ligands afford widely space for the development of potential applied molecular-based materials with topological structures and interesting physical properties such as magnetism, photonics, electricity and catalysis as well as multi-functional properties^[7-10].

As one important type of numerous ligands, the pyridine carboxamide ligands containing ubiquitous carboxamide [-C(O)NH-] groups and pyridine rings have also received much interests^[11-24]. The pyridine carboxamide ligands can be easily available usually through the condensation of pyridine carboxylic acids and amines, and then they can be employed as multi-chelate negative ligands after the deprotonation of the carboxamide nitrogen atom. To date, many complexes in which carboxamide-based organic compounds usually are employed as tri- or tetra-dentate in-plane chelate ligands have been reported. To our knowledge there are still no reports on the complexes bridged by the carboxamide nitrogen atom as bridging group. Moreover, the compounds with twisted pyridine carboxamide ligands are very limited. Recently, we unexpectedly obtained a carboxamide nitrogen-bridged binuclear cobalt(III) complex $[\text{Co}_2(\text{bpmp})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ with twisted pyridine carboxamide ligands and cyanide groups when we try to assembly cyanato-bridged binuclear manganese(II) complex according to the

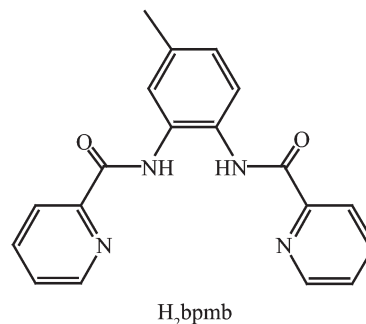
induction mechanism of the large anion reported previously^[25]. Herein, we report the synthesis and crystal structure of the complex.

1 Experimental

1.1 Materials and physical measurements

All starting materials were purchased commercially and were of analytical reagent grade.

The precursors $\text{K}[\text{Co}(\text{bpmb})(\text{CN})_2]$ ^[13] and $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ ^[26] were prepared according to literature methods. IR (KBr pellets) for $\text{K}[\text{Cr}(\text{bpmb})(\text{CN})_2]$: 2 132 (w, $\nu_{\text{C}\equiv\text{N}}$), 2 070 (w, $\nu_{\text{C}\equiv\text{N}}$), 1 627 (vs, $\nu_{\text{C}=\text{O}}$), 1 594 (vs), 1 575 (vs), 1 561 (s), 1 472 (s), 1 367 (vs), 1 293 (m), 963 (m), 760 (s), 693 (m), 518 (m) cm^{-1} .



Elemental analyses of carbon, hydrogen and nitrogen were carried out with an Elementary Vario El. The IR spectra with KBr pellets were recorded on a Magna-IR 750 spectrophotometer in the 4 000 ~400 cm^{-1} regions.

1.2 Synthesis of $[\text{Co}_2(\text{bpmp})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ (1)

Brown block single crystals suitable for X-ray diffraction analysis of the title complex were obtained by slow reaction in a mixture prepared by carefully mixing $\text{CH}_3\text{CN}-\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solution (5 mL) of $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ (0.1 mmol), CH_3OH solution (5 mL) of $\text{K}[\text{Co}(\text{bpmb})(\text{CN})_2]$ (0.1 mmol) and aqueous solution (2 mL) of NaNCO (0.6 mmol) at room temperature. At the same time, yellow block single crystals of by-product $[\text{Mn}(\text{phen})(\text{NCO})_2]$ produced. These crystals were separated manually under microscope. Yield: 3% for **1** and 25% for $[\text{Mn}(\text{phen})(\text{NCO})_2]$. IR (KBr pellet) for **1**: 2 134 (w, $\nu_{\text{C}\equiv\text{N}}$), 2 072 (w, $\nu_{\text{C}\equiv\text{N}}$), 1 617 (vs, $\nu_{\text{C}=\text{O}}$), 1 591 (vs), 1 555 (vs), 1 471 (s), 1 368 (vs), 1 293 (m), 965 (m), 754 (s), 687 (m), 515 (s) cm^{-1} . Element analysis: calcd. for $\text{Co}_2\text{C}_{40}\text{H}_{30}\text{N}_{10}\text{O}_5$ (%): C, 56.56; H, 3.61; N, 16.51; found (%): C,

56.89; H, 3.26; N, 16.78.

1.3 X-ray crystallographic study

Determination of unit cell and data collection of the complex was performed on a Bruker SMART APEX II CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature. The structure was solved by the direct method with SHELXS-97 and refined by full matrix least-squares with SHELXL-97 on F^2 . All non-hydrogen atoms were

refined with anisotropic thermal parameters, and hydrogen atoms attached to C atoms were added geometrically and refined using a riding model position parameters and fixed isotropic thermal parameters. The water hydrogen atoms were found from the E-map, and refined isotropically. Further details of the structure analysis for the title complex are given in Table 1.

CCDC: 661715.

Table 1 Crystallographic data for complex **1**

Empirical formula	$\text{Co}_2\text{C}_{40}\text{H}_{30}\text{N}_{10}\text{O}_5$	Max. and Min. Transmission	0.907, 0.941
Formula weight	848.6	$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.618
Wavelength / nm	0.071 073	$F(000)$	1 736
Crystal system	Monoclinic	θ range for data collection / ($^\circ$)	3.01~25.00
Space group	$P2_1/c$	Reflections collected / unique	22 777 / 5 925
a / nm	1.512 0(3)	R_{int}	0.044 3
b / nm	1.536 4(3)	Data / restraints / params	5 925 / 3 / 508
c / nm	1.501 3(3)	Reflections with $I > 2\sigma(I)$	5 140
β / ($^\circ$)	92.97(3)	Goodness-of-fit on F^2	1.102
V / nm^3	3.482 9(12)	R_1 ($I > 2\sigma(I)$)	0.070 3
Z	4	wR_2 (all data)	0.163 1
Absorption coefficient / mm^{-1}	1.017		

2 Results and discussion

2.1 Synthesis

With the original intent of assembling cyanato-bridged dimeric manganese(II) complexes based on the induction mechanism of large anion $[\text{Co}(\text{bpmb})(\text{CN})_2]^-$ ^[25], we investigated the reactions of $[\text{Co}(\text{bpmb})(\text{CN})_2]^-$ with $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ under the presence of NaNCO. Unexpectedly single crystals of binuclear Co(III) complex $[\text{Co}_2(\text{bpmp})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ suitable for single crystal structural analysis were obtained. However, there is no complex **1** without $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ or NaNCO in the reaction system. In general, the formation mechanism of **1** is very complicated. Herein, we only briefly analyze the formation of **1** from the stability of the precursors and products. According to our previously results^[24], the cyanide- or azide-containing building blocks with the pyridine carboxamide ligand bpb^{2-} such as $\text{K}[\text{Cr}(\text{bpb})(\text{CN})_2]$ and $\text{K}[\text{Cr}(\text{bpb})(\text{N}_3)_2]$ are usually unstable in the presence of metal ions or some unsaturated metal complexes, yielding more stable monomeric complexes

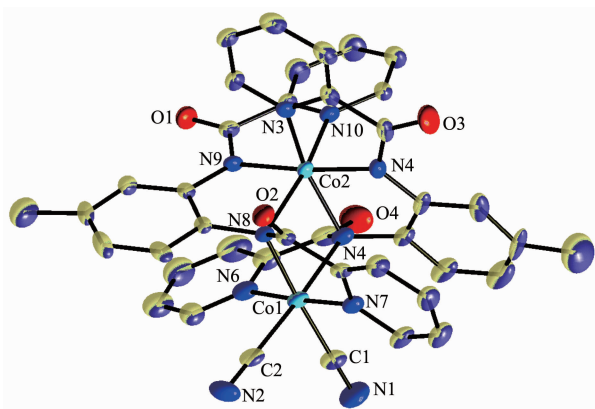
$[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{OH})]$ and $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{N}_3)]$, respectively. We attribute the formation of $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{OH})]$ and $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{N}_3)]$ to $\text{K}[\text{Cr}(\text{bpb})(\text{CN})_2]$ and $\text{K}[\text{Cr}(\text{bpb})(\text{N}_3)_2]$ are unstable and the $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{OH})]$ and $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{N}_3)]$ are more stable than their precursors. Similarly, the formation of complex **1** can partly be due to that $\text{K}[\text{Co}(\text{bpmb})(\text{CN})_2]$ are not stable in the reaction system and there exist dissociation reaction of cyanide groups and the ion compound $\text{K}[\text{Co}(\text{bpmb})(\text{CN})_2]$ is more soluble than the neutral complex **1** in this system. The formation of the by-product $[\text{Mn}(\text{phen})_2(\text{NCO})_2]$ is natural and it is also one of the reasons for low yield of **1**. The roles of NaNCO and $[\text{Mn}(\text{phen})_2\text{Cl}_2]$ in the system and the induction factor of ligand bpmb^{2-} twisting in **1** still need further study.

2.2 Crystal structure

The geometry and labeling scheme for the crystal structures of $[\text{Co}_2(\text{bpmp})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ is depicted in Fig. 1, and some selected bond lengths and angles are presented in Table 2. In the molecular structure, the pyridine carboxamide ligand H_2bpmb forms tetradentate

Table 2 Selected bond distances (nm) and angles (°) of complex **1**

Co(1)-C(1)	0.190 2(6)	Co(2)-N(3)	0.194 0(5)	Co(1)-C(2)	0.189 6(6)
Co(2)-N(4)	0.189 1(4)	Co(1)-N(5)	0.201 7(4)	Co(2)-N(5)	0.203 2(4)
Co(1)-N(6)	0.193 4(5)	Co(2)-N(8)	0.202 1(4)	Co(1)-N(7)	0.192 2(5)
Co(2)-N(9)	0.188 9(4)	Co(1)-N(8)	0.201 0(5)	Co(2)-N(10)	0.194 0(4)
N(1)-C(1)	0.114 1(7)	N(2)-C(2)	0.115 2(7)	Co(1)···Co(2)	0.299 0(6)
Co(1)-N(8)-Co(2)	95.78(18)	Co(1)-N(5)-Co(2)	95.20(18)	N(5)-Co(1)-N(8)	84.78(17)
C(1)-Co(1)-C(2)	89.0(2)	N(1)-C(1)-Co(1)	178.2(4)	N(2)-C(2)-Co(1)	177.4(5)
C(1)-Co(1)-N(5)	176.8(2)	C(2)-Co(1)-N(8)	177.1(2)	N(7)-Co(1)-N(6)	176.62(19)
N(3)-Co(2)-N(5)	165.94(19)	N(9)-Co(2)-N(4)	174.76(19)	N(10)-Co(2)-N(8)	163.94(18)



Lattice water molecule and hydrogen atoms have been omitted for clarity

Fig.1 ORTEP drawing of complex **1** with thermal ellipsoids at 30% probability level

chelate ligand bpmb^{2-} with two negative charges after the deprotonation of the carboxamide nitrogen atoms. It is noteworthy that the usually in-plane ligand bpmb^{2-} twists and coordinates two Co(III) ions with carboxamide nitrogen as bridging atom in the title complex.

The Co(1) ion in $[\text{Co}_2(\text{bpmp})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ is six-coordinated by two pyridine nitrogen, two bridging carboxamide nitrogen atoms from two bpmb^{2-} ligands, and two *cis*-cyanide carbon atoms, giving a distorted octahedral CoN_4C_2 environment. The $\text{Co}-\text{C}_{\text{cyanide}}$ bond distances are 0.190 2(6) and 0.189 6(6) nm for Co(1)-C(1) and Co(1)-C(2), respectively. The average bond distances of Co(1)- $\text{N}_{\text{pyridine}}$ (0.192 9(5) nm) is significantly shorter than that of the average bond distances of Co(1)- $\text{N}_{\text{bridging-amide}}$ (0.201 3(4) nm), which is very different from those of $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{OH})] \cdot 3\text{H}_2\text{O}$ ^[24], $[\text{Cr}(\text{bpb})(\text{H}_2\text{O})(\text{N}_3)] \cdot \text{H}_2\text{O}$ ^[24], $[\text{Co}^{\text{III}}(\text{bpb})\text{Et}(\text{H}_2\text{O})]$ ^[13], $[\text{Cr}(\text{bpb})\text{N}]$ ^[14], $\text{Na}[\text{Fe}^{\text{III}}(\text{bpb})(\text{N}_3)_2]$ ^[15], $\text{Na}[\text{Fe}^{\text{III}}(\text{bpb})(\text{CN})_2]$ ^[15], and $[\text{Fe}^{\text{III}}(\text{bpc})$

$\text{Cl}(\text{DMF})]$ ^[16], even dimeric complexes $[\text{Fe}^{\text{IV}}_2(\mu\text{-N})(\text{bpb})_2(\text{CN})_2]$ ^[15] and $[\text{Fe}^{\text{IV}}_2(\mu\text{-N})(\text{bpb})_2(\text{N}_3)_2]$ ^[15] and many clusters and polymers^[8-10,22,24-25] containing large in-plane pyridine carboxamide ligands because the amide nitrogen atoms in the title complex play the role of bridges other than only as coordination atoms. The C-N bond distances are 0.114 1(6) and 0.115 2(6) nm for C(1)-N(1) and C(2)-N(2), respectively, which are in fashion. The $\text{Co}-\text{C}\equiv\text{N}$ bond angles are nearly strict linear ($178.2(4)^\circ$ for Co(1)-C(1)-N(1) and $177.4(5)^\circ$ for Co(1)-C(2)-N(2)). The bond angles $\text{N}_{\text{pyridine}}\text{-Co(1)-N}_{\text{pyridine}}$ is $176.62(19)^\circ$ for N(6)-Co(1)-N(7), the $\text{N}_{\text{amide}}\text{-Co(1)-N}_{\text{amide}}$ is $84.78(17)^\circ$ for N(5)-Co(1)-N(8) and the $\text{C}_{\text{cyanide}}\text{-Co(1)-C}_{\text{cyanide}}$ is $89.0(2)^\circ$ for C(1)-Co(1)-C(2). The dihedral angle between the two pyridine rings around Co(1) ion is $76.2(2)^\circ$.

The Co(2) ion in the title complex is six-coordinated by two pyridine nitrogen, two unbridging carboxamide nitrogen and two bridging carboxamide nitrogen atoms from two bpmb^{2-} ligands yielding a significantly distorted octahedral CoN_6 geometry evidenced due to the increased strain exerted by the two twisted bpmb^{2-} ligand as evidenced by the angles N(3)-Co(2)-N(5) of $165.94(19)^\circ$, N(9)-Co(2)-N(4) of $174.76(19)^\circ$ and N(10)-Co(2)-N(8) of $163.94(18)^\circ$. The averaged Co(2)- $\text{N}_{\text{bridging-amide}}$ bond distance (0.203 0(4) nm) is significantly longer than those of Co(2)- $\text{N}_{\text{pyridine}}$ (0.194 5(4) nm) and Co(2)- $\text{N}_{\text{unbridging-amide}}$ (0.188 5(4) nm). The bridging angles of Co(1)- $\text{N}_{\text{bridging-amide}}\text{-Co(2)}$ is $95.78(18)^\circ$ for Co(1)-N(8)-Co(2) and $95.20(18)^\circ$ Co(1)-N(5)-Co(2), respectively. The intramolecular metal separation is 0.399 0(6) nm for Co(1)···Co(2). The twisted angles of the two bpmb^{2-} ligands in the title compound are about 75° and 80° ,

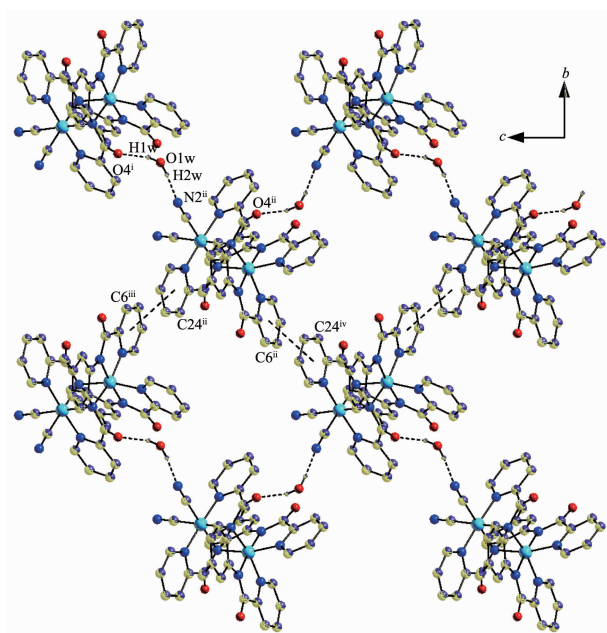
respectively.

Fig.2 displays the unit packing diagrams of complex $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ along the a and b axis. The $[\text{Co}_2(\text{bpmb})_2(\text{CN})_2] \cdot \text{H}_2\text{O}$ units form zigzag one-dimensional chains through two hydrogen bonds involving caboxamide oxygen (O4), cyanide nitrogen (N2) and free water molecule oxygen atoms as listed in Table 3. The chains are further linked together by

Table 3 Hydrogen bonds in 1

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
O1W-H1W...O4 ⁱ	0.084 5	0.208 5	0.290 9(5)	164.82
O1W-H2W...N2 ⁱⁱ	0.084 7	0.201 7	0.285 7(5)	171.28

Symmetry codes: ⁱ $-x+1, y+1/2, -z+3/2$; ⁱⁱ $-x+1, -y, -z+1$.



Symmetry code: ⁱ $-x+1, y+1/2, -z+3/2$; ⁱⁱ $-x+1, -y, -z+1$; ⁱⁱⁱ $-x+1, +y-1/2, -z+1/2$; ^{iv} $-x+1, +y+0.5, -z+0.5$

Fig.2 Two-dimensional layer-like structure through the hydrogen bonds π - π interactions and in complex 1 in the bc plane

2.3 Spectroscopic properties

The IR spectra of the title complex in the range $2000 \sim 200 \text{ cm}^{-1}$ show two weak peaks, indicating the presence of two different cyanide ligands in the complex. The IR spectra of 1 in the range of $1650 \sim 500 \text{ cm}^{-1}$ are very similar with those of their precursors $\text{K}[\text{Co}(\text{bpmb})(\text{CN})_2]^-$, suggesting the pyridine carboxamide ligand bpmb^{2-} exists in the title complex. The IR analyses for the complex are well consistent with the

intermolecular π - π packing interactions with the shortest distance of $0.335 2(6) \text{ nm}$ between adjacent pyridine rings into a two-dimensional network supramolecular structure. It is noteworthy that there exists relative strong intramolecular π - π interaction between pyridine and benzene rings from two bpmb^{2-} ligands in complex 1.

crystal structure analysis results.

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