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Introduction

Metal–organic frameworks (MOFs) from organic ligands and transition metals have become a field of rapid growth in supramolecular and material chemistry due to their intriguing structural diversity¹ and potential applications in the fields of fluorescence,² magnetism,³ catalysis⁴ and host–guest chemistry.⁵ For researchers, the construction of coordination compounds is still a big challenge because the self-assembly of metal ions and ligands into coordination architectures is not easily controlled. In crystal engineering, the metal centers are important connecting nodes in multidimensional arrays due to their varied coordinating models. Organic ligands are

Cobalt(II), copper(II), zinc(II) and cadmium(II) complexes based on dibenzimidazolyl bidentate ligands with alkanyl linkers: crystal structure, weak interactions and conformations†

Qing-Xiang Liu,^{*a,b} Qing Wei,^{a,b} Xiao-Jun Zhao,^{a,b} Hong Wang,^{a,b} Shu-Juan Li^{a,b} and Xiu-Guang Wang^{a,b}

Eight metal complexes, {[Co(bibim-4)₂(H₂O)₂](NO₃)₂, (1), {[Cu(bibim-4)₂(NO₃)](NO₃)₂, (2), [Co(bibim-3)-(TP)]_n (3), [Zn₂(bibim-3)]₂(OAc)₄] (4), [Co(bibim-2)(NO₃)₂]_n (5), [Zn(bibim-4)(NO₃)₂]_n (6), [Zn(bibim-4)-(OAc)₂]_n (7) and [Cd(bibim-4)(NO₃)₂(DMF)]_n (8) (bibim-2 = 1,2-bis(benzimidazol-l-yl)ethane, bibim-3 = 1,3-bis(benzimidazol-l-yl)propane, bibim-4 = 1,4-bis(benzimidazol-l-yl)butane and TP = terephthalate) have been prepared by means of the self-assembly of Co(II), Cu(II), Zn(II) or Cd(II) salts, dibenzimidazolyl bidentate ligands bearing alkanyl linkers and terephthalic acid. These complexes are structurally characterized by X-ray diffraction analyses. In complexes 1 and 2, 2D network layers with macrometallocycles in 3 is formed *via* metal centers and the ligand bibim-4. A 2D network layer with macrometallocycles in 3 is formed *via* Co(II) centers, the ligand bibim-3 and terephthalate molecules. In complexes 5–8, 1D polymeric chains are formed *via* metal centers and the bibim-2 or bibim-4 ligands. In the crystal packings of complexes 1–8, 2D supra-molecular layers and 3D supramolecular frameworks are formed *via* intermolecular weak interactions, including π - π interactions and hydrogen bonds. The different types of π - π interactions from the benzimidazole, the ligands and metal complexes are described. Additionally, the fluorescence emission spectra of the ligands and metal complexes are reported.

important building blocks to construct coordination frameworks of diverse sizes and shapes. Furthermore, organic diacids (like terephthalic acid) are often used together with other organic ligands in order to form some porous coordination architectures. Among the family of organic ligands, ligands bearing N-donors are a type of important ligating moiety connecting the metal atoms and their N-donor units contain mainly pyridine,⁶ benzimidazole,⁷ imidazole,⁸ triazole,⁹ pyrrole¹⁰ and imino groups.¹¹

Bidentate ligands with different linkers are usually the typical building elements in multidimensional networks in which non-rigid linkers, such as polyether chains,¹² polyimino chains¹³ and alkyl chains¹⁴ may provide a greater possibility for the construction of unusual coordination frameworks due to the conformationally flexible nature of the bidentate ligands. Therefore, the design and synthesis of new bidentate ligands are important for crystal engineering. Additionally, among the ligands containing nitrogen atoms, imidazolyl (or benzimidazolyl) ligands have prominent importance because the imidazole ring is a structural component of many compounds occurring in living organisms.¹⁵ In the mechanisms of

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^aTianjin Key Laboratory of Structure and Performance for Functional Molecules, Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, Ministry of Education, College of Chemistry, Tianjin Normal University, Tianjin 300387, China ^bState Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, China. E-mail: tjnulqx@163.com

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the majority of enzymatic reactions, metal complexes based on imidazole play important roles in physiology.¹⁶ Therefore, the preparation and investigating the structure of metal complexes from imidazolyl (or benzimidazolyl) has great significance toward knowing the coordinating process between the imidazole (or benzimidazolyl) ring and metal ions in life science.

So far, a lot of metal complexes based on diimidazolyl bidentate ligands with different alkanyl linkers have been reported,¹⁷⁻²⁶ but only a few examples of metal complexes based on dibenzimidazolyl bidentate ligands with a 1,4-butene linker have been described.^{27–29} The main difference of dibenzimidazolyl bidentate ligands in contrast to diimidazolyl bidentate ligands is that the conjugated system of the benzimidazole ring is bigger than that of the imidazole ring and the benzimidazole ring participates in π - π interactions between molecules more easily. π - π interactions, along with other weak interactions (like hydrogen bonds), can provide more opportunities for constructing supramolecular architectures. Additionally, π - π stacking interactions also play an important role in stabilizing supramolecular architectures.^{28,30} In order to further understand the structure of metal complexes based on dibenzimidazolyl bidentate ligands with different alkanyl linkers, we here report the preparation of three dibenzimidazolyl bidentate ligands, 1,2-bis(benzimidazol-l-yl)ethane (bibim-2), 1,3-bis(benzimidazol-l-yl)propane (bibim-3) and 1,4-bis-(benzimidazol-l-yl)butane (bibim-4), as well as the preparation, structures and fluorescence emission spectra of eight metal complexes, $\{[Co(bibim-4)_2(H_2O)_2](NO_3)_2\}_n$ (1), $\{[Cu(bibim-4)_2 (NO_3)$ (NO_3) $_n$ (2), $[Co(bibim-3)(TP)]_n$ (3), $[Zn_2(bibim-3)]_2(OAc)_4$ (4), $[Co(bibim-2)(NO_3)_2]_n$ (5), $[Zn(bibim-4)(NO_3)_2]_n$ (6), $[Zn-2)(NO_3)_2]_n$ (6), $[Zn-2)(NO_3)_2]_n$ (6), $[Zn-2)(NO_3)_2]_n$ (7) $(bibim-4)(OAc)_2]_n$ (7) and $[Cd(bibim-4)(NO_3)_2(DMF)]_n$ (8) (TP = terephthalate). Additionally, the conformations of the ligands and metal complexes are described.



Results and discussion

Synthesis and characterization of the ligands (bibim-*m*) and metal complexes 1–8

The bis-benzimidazole ligands 1,2-bis(benzimidazol-l-yl)ethane (**bibim-2**), 1,3-bis(benzimidazol-l-yl)propane (**bibim-3**) and 1,4bis(benzimidazol-l-yl)butane (**bibim-4**) were prepared through the reaction of benzimidazole with 1,*m*-dibromoalkane (m = 2, 3 and 4). The ligands (**bibim-m**) are white powders and they are soluble in common organic solvents (such as CH₃OH, CH₃CN and DMF). In contrast to the diimidazolyl bidentate ligands, the solubility of dibenzimidazolyl bidentate ligands in water is slightly poorer. During the course of the preparation of metal complexes using dibenzimidazole with alkanyl linkers as a ligand, using only water as the solvent is not suitable. Using water and an organic solvent as a mixed solvent or only using organic solvents is necessary. Thus, the crystallization of complexes from dibenzimidazolyl bidentate ligands and inorganic metal salts occurs readily in the appropriate solvent.

Complexes {[Co(bibim-4)₂(H₂O)₂](NO₃)₂}_n (1), {[Cu(bibim-4)₂(NO₃)](NO₃)}_n (2), [Zn₂(bibim-3)]₂(OAc)₄] (4), [Co(bibim-2)-(NO₃)₂]_n (5), [Zn(bibim-4)(NO₃)₂]_n (6), [Zn(bibim-4)(OAc)₂]_n (7) and [Cd(bibim-4)(NO₃)₂(DMF)]_n (8) were prepared *via* the reaction of **bibim-m** with the metal salts (Co(NO₃)₂·6H₂O for 1 and 5, Cu(NO₃)₂·3H₂O for 2, Zn(OAc)₂·2H₂O for 4 and 7, Zn-(NO₃)₂·6H₂O for 6 and Cd(NO₃)₂·4H₂O for 8) in DMF-CH₃OH, while complex [Co(bibim-3)(TP)]_n (3) was prepared *via* the reaction of **bibim-3** and terephthalic acid with Co(NO₃)₂·6H₂O in the presence of Et₃N in DMF-CH₃OH. Crystals of 1–8 suitable for X-ray diffraction were grown by slowly evaporating the DMF-CH₃OH solution at room temperature. Complexes 1–8 are stable and can retain their structural integrity at room temperature for a considerable length of time.

Structure of complexes 1-8

Complexes 1 and 2 have similar 2D network layers with quadrangle cavities, as shown in Fig. 1(a) and 2(a). The adjacent quadrangle cavities are connected *via* metal atoms (Co(II) for 1 and Cu(II) for 2). Each quadrangle cavity of central symmetry is formed by four bis-benzimidazole **bibim-4** ligands and two metal atoms. In the quadrangle cavities of 1 and 2, the adjacent distances of M····M are 13.757(1) Å for the Co···Co of 1 and 11.757(2) Å for the Cu···Cu of 2 and the distances of opposite M····M are 16.916(2) Å for the Co···Co of 1 and 23.178(3) Å for the Cu···Cu of 2. In complexes 1 and 2, the dihedral angles of two benzimidazole rings within the same ligand are $0.6(1)^{\circ}$ for 1 and $11.0(1)^{\circ}$ for 2. The benzimidazole ring and other three benzimidazole rings linked to the same metal center form dihedral angles of $68.5(1)^{\circ}$, $51.6(1)^{\circ}$ and $80.3(1)^{\circ}$ for 1 and $90.2(1)^{\circ}$, $88.8(1)^{\circ}$ and $90.6(1)^{\circ}$ for 2.

In complex 1, each Co(II) atom is surrounded by four nitrogen atoms from four bis-benzimidazole **bibim-4** ligands and two oxygen donors from two water molecules to adopt an octahedral geometry. The axial positions of the octahedron are occupied by O(1) and O(2) with an O(1)–Co(1)–O(2) angle of 180°. The bond distances of Co(1)–O(1) and Co(1)–O(2) are 2.191(5) Å and 2.066(4) Å, respectively. Four N(1), N(1A), N(3) and N(3A) atoms lie in the equatorial plane. The distances of the Co–N bond are from 2.132(4) Å to 2.161(3) Å. The bond angle of N–Co–O is in the ranges of 87.2(2)° to 92.7(8)°. The bond angles of N(1)–Co(1)–N(1A) and N(3)–Co(1)–N(3A) are 177.1(2)° and 174.4(5)°, respectively. These values are favorably comparable with other analogous imidazole derivatives of Co(II).³¹

In complex 2, each Cu(π) atom is surrounded by four nitrogen donors from four bis-benzimidazole **bibim-4** ligands and one oxygen donor from a nitrate group to adopt a pentagonal pyramidal geometry. The bond angles of N–Cu–N are in the ranges of 88.6(5)° to 170.3(9)° and the bond angles of N–Cu–O







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Fig. 1 (a) 2D layer of 1. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–O(1) 2.191(5), Co(1)–O(2) 2.066(4), Co(1)– N(1) 2.161(3), Co(1)-N(3) 2.132(4); O(2)-Co(1)-N(3) 92.7(8), O(2)-Co(1)-N(1) 91.4(4), N(1)-Co(1)-N(3) 89.1(8), O(1)-Co(1)-O(2) 180.0(0), N(3)-Co(1)-O(1) 87.2(2), N(1)-Co(1)-O(1) 88.5(6), N(1)-Co(1)-N(1A)ⁱ 177.1(2), N(3)-Co(1)-N(3A)ⁱ 174.4(5). Symmetry code: i: 2 - x, 2 - y, 1 - z. (b) 3D supramolecular frameworks of 1 formed by interlayer O-H···O hydrogen bonds. All hydrogen atoms except those participating in the O-H…O hydrogen bonds were omitted for clarity. Symmetry code: ii: 1/2 + x, 1 - y, 1/2 + z; iii: 1 - x, 1 - y, 2 - z; iv: 3 - x, 1 - y, 2 - z.

are in the ranges of 92.8(9)° to 96.7(1)°. These values are within the normal ranges.³²

In complex 3, a 2D network layer with 56-membered hexagon cavities of central symmetry is formed by two relatively little 20-membered rings, four terephthalates (TP) and six Co(II) atoms, as shown in Fig. 3(a). The size of the 56-membered hexagon cavity is ca. 18.691(2) Å \times 7.413(9) Å. In the hexagon cavity, the two pairs of opposite benzene rings from the terephthalate molecules are parallel to each other, respectively, with separations of 14.292(1) Å and 20.328(1) Å. The Co…Co distance at two ends of the terephthalate molecule is 11.013(1) Å. The dihedral angle between two benzene rings of terephthalate connected to the same $Co(\pi)$ center is $80.2(1)^{\circ}$. The dihedral angles between one benzimidazole ring and two benzene rings of the terephthalate molecule connected to the same $Co(\pi)$ atom are 110.6(1)° and 128.7(9)°, respectively.

Fig. 2 (a) 2D layer of 2. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.019(4), Cu(1)–N(8)ⁱ 2.001(4), Cu(1)– N(4)ⁱⁱ 1.992(4), Cu(1)–N(5) 2.014(4), Cu(1)–O(1) 2.352(4); N(1)–Cu(1)–N(5) 88.7(6), N(1)-Cu(1)-N(4) 169.9(5), N(5)-Cu(1)-N(8) 170.3(9), N(1)-Cu(1)-O(1) 93.6(5), N(4)-Cu(1)-O(1) 96.1(8). N(5)-Cu(1)-O(1) 92.8(9). Symmetry code: i: 3/2 - x, -1/2 + y, -1/2 + z; ii: 3/2 - x, 1/2 + y, -1/2 + z. (b) 3D supramolecular frameworks of 2 formed by interlayer C-H···O hydrogen bonds. All hydrogen atoms except those participating in the C-H--O hydrogen bonds were omitted for clarity. Symmetry code: iii: 1 - x, -y, 1/2 + z.

Each relatively small 20-membered ring in 3 is formed by two bis-benzimidazole **bibim-3** ligands and two $Co(\pi)$ atoms, in which the dihedral angle between two benzimidazole rings within the same ligand is nearly perpendicular with a dihedral angle of 87.7(1)° and the dihedral angle of two benzimidazole rings connected to the same Co(II) atom is $88.7(1)^\circ$. The Co…Co distance in the 20-membered rings is 9.748(1) Å. The size of the 20-membered ring of central symmetry is ca. 9.748(1) Å \times 5.806(6) Å.

Interestingly, each acetone molecule in 3 is connected to an uncoordinated oxygen atom of the carboxyl group via C-H···O hydrogen bonds (the data of the hydrogen bonds is given in Table 1). In the hydrogen bonds, the hydrogen atoms are from the CH₃ of acetone and the oxygen atoms are from the carboxyl group. As a result, each 56-membered hexagon cavity includes two acetone molecules. Analysis of the crystal structure of 3 reveals that each Co(II) center adopts a distorted tetrahedral



Fig. 3 (a) 2D layer of **3**. All hydrogen atoms except those participating in the C–H···O hydrogen bonds were omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–O(1) 1.963(5), Co(1)–O(3) 1.950(8), Co(1)–N(1) 2.012(7), Co(1)–N(1A) 2.012(7); O(1)–Co(1)–O(3) 105.3(3), O(3)–Co(1)–N(1) 128.5(3), O(1)–Co(1)–N(1) 110.6(3), N(1)–Co(1)–N(1A)¹ 102.5(2). Symmetry code: i: 1 - x, 2 - y, 1 - z; ii: x, 1 + y, 1 + z. (b) 3D supramolecular frameworks of **3** *via* weak π – π interactions. All hydrogen atoms were omitted for clarity.

Table 1 H-bonding geometry (Å, °) for complexes 1-8

Compounds	D–H···A	D-H	Н…А	D····A	D-H···A
1	$O(1)-H(1A)\cdots O(6)^{ii}$ $O(2)^{iv}-H(2A)\cdots O(7)^{iii}$	0.85(1) 0.85(1)	1.977(2) 1.877(2)	2.814(3) 2.711(3)	168.0(1) 166.7(1)
2 3	$O(7)-H(7B)\cdots O(6)^{a}$ $C(25)-H(25)\cdots O(2)^{a}$ $C(31)-H(31A)\cdots O(4)^{a}$	$\begin{array}{c} 0.85(2) \\ 0.93(4) \\ 0.96(1) \end{array}$	$\begin{array}{c} 1.944(2) \\ 2.440(4) \\ 1.898(2) \end{array}$	$\begin{array}{c} 2.794(3) \\ 3.329(6) \\ 2.805(3) \end{array}$	177.0(1) 159.7(2) 156.6(1)
4 5 6	$C(8)-H(8A)\cdots O(4)^{ii}$ $C(9)-H(9)\cdots O(3)^{ii}$ $C(1)-H(1)\cdots O(5)^{ii}$	0.97(1) 0.93(4) 0.93(1)	2.437(1) 2.463(9) 2.375(1)	3.308(2) 3.376(1) 3.158(2)	149.2(4) 167.2(4) 141.7(2)
7 8	$C(8) - H(8B) \cdots O(4)^{i}$ $C(7) - H(7) \cdots O(3)^{ii}$	0.97(1) 0.93(1)	$2.592(3) \\ 2.555(3)$	3.420(4) 3.413(4)	$143.5(1) \\153.4(1)$

Symmetry code: ii: 1/2 + x, 1 - y, 1/2 + z. iii: 1 - x, 1 - y, 2 - z. iv: 3 - x, 1 - y, 2 - z for 1. iii: 1 - x, -y, 1/2 + z for 2. ii: x, 1 + y, 1 + z for 3. ii: x, 2 - y, -1/2 + z for 4. i: x, 1/2 - y, 1/2 + z for 5. i: 1 - x, 2 - y, 2 - z for 6. i: 2 - x, 1 - y, 1 - z for 7. ii: 1/2 - x, 1/2 - y, 1 - z for 8.

geometry formed by two oxygen donors from two different carboxyls (the Co–O distances vary from 1.950(8) Å to 1.963(5) Å) and two nitrogen donors from two benzimidazole rings (the Co–N distance is 2.012(7) Å). The bond angles of O(1)–Co(1)– O(3) and N(1)–Co(1)–N(4A) are 105.3(3)° and 102.6(3)°, respectively. The bond angle of O–Co–N is in the range of $102.4(3)^{\circ}$ to $128.5(3)^{\circ}$. These values are comparable with those of complex 1 and the reported Co(II) complexes.³³

In complex 4 (Fig. 4(a)), one 20-membered macrometallocycle is formed by two didentate **bibim-3** ligands and two Zn(II) atoms, in which the dihedral angle of two benzimidazole rings connected to the same Zn(II) atom is 84.8(1)° and the dihedral angle of two benzimidazole rings within the same ligand is 84.6(1)°. Each Zn(II) atom is surrounded by two nitrogen donors from two benzimidazole rings and two oxygen donors from two acetate groups to adopt a distorted tetrahedral geometry. The bond distances of Zn(1)–O(1) and Zn(1)–N(1) bond are 1.949(4) Å and 2.007(2) Å, respectively. The bond angles of O(1)–Zn(1)–O(3) and N(1)–Zn(1)–N(4A) are 109.7(4)° and 101.9(4)°, respectively. The bond angles of O–Zn–N range from 102.3(7)° to 120.9(8)°. These values are consistent with those from published Zn(II) complexes.³²

1D zigzag polymeric chains of complexes 5–8 are formed *via* didentate ligands and metal atoms (**bibim-2** and Co(II) for 5, **bibim-4** and Zn(II) for 6 and 7, **bibim-4** and Cd(II) for 8) (Fig. 5(a)–8(a)). The two benzimidazole rings connected to the same metal center form dihedral angles of $83.9(3)^{\circ}$ for 5, 64.8° for 6, 55.7° for 7 and $81.1(4)^{\circ}$ for 8. Two benzimidazole rings within the same ligand are parallel for 5–8. In 5, the neighboring Co…Co separation is 11.613(4) Å and the angle of the neighboring Co…Co is $84.6(4)^{\circ}$. In 6 and 7, the neighboring 7 and the angles of the neighboring Zn…Zn separation is 11.940(6) Å for 6 and 11.915(1) Å for 7 and $81.2(5)^{\circ}$ for 7. In 8, the neighboring Cd…Cd separation is 12.338(1) Å and the angle of the neighboring Cd…Cd is $112.3(1)^{\circ}$.

In complex 5, the hexa-coordinated Co(II) atom is surrounded by two nitrogen donors from two benzimidazole rings and four oxygen donors from two nitrate groups to adopt a distorted octahedral geometry. The axial positions of the octahedron are occupied by N(1) and O(2) with axial distances of 4.044(1) Å and a N(1)–Co(1)–O(2) angle of 140.3(3). Four N(3), O(1), O(4) and O(5) atoms lie in the equatorial plane. The bond distances of Co–O range from 2.155(9) Å to 2.390(1) Å, and Co–N distances are 2.005(6) Å and 2.018(6) Å, respectively. The N(1)–Co(1)–N(3) bond angle is 105.6(2)° and the value of the bond angles around the Co(II) center varied from 52.1(3)° to 140.3(3)°. These values are favorably comparable with those of complexes 1 and 3 and the reported Co(II) complexes.³¹

In complexes 6 and 7, each Zn(II) atom is surrounded by two nitrogen donors from two benzimidazole rings and two oxygen donors (from two nitrite groups for 6 and from two acetate groups for 7) to form a distorted tetrahedral geometry. The distances of Zn–O are from 1.926(5) Å to 1.963(5) Å and the distances of Zn–N are from 2.005(7) Å to 2.040(3) Å. The bond angles of O–Zn–O are from 110.0(9)° to 113.4(9)°, the bond angles of N–Zn–N are from 103.1(1)° to 111.6(8)° and the bond angles of O–Zn–N range from 96.2(0)° to 119.1(7)°. These values fall in the normal ranges of Zn(II) complexes.^{31,34}

There is a solvent accessible void in the unit cell of complexes 6 or 7. Each unit cell of 6 contains one disordered water







(b)







Fig. 4 (a) Perspective view of **4** and the anisotropic displacement parameters depicting 50% probability. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 1.949(4), Zn(1)–O(3) 1.958(5), Zn(1)–N(1) 2.007(2), Zn(1)–N(4A)ⁱ 2.054(2); O(1)–Zn(1)–O(3) 109.7(4), O(1)–Zn(1)–N(1) 121.9(8), O(1)–Zn(1)–N(4A) 106.3(5), O(3)–Zn(1)–N(1) 113.1(6), O(3)–Zn(1)–N(4A) 102.3(7), N(1)–Zn(1)–N(4A) 101.9(4). Symmetry code: i: 1/2 – *x*, 3/2 – *y*, –*z*. (b) 2D supramolecular layer of **4** formed *via* C–H···O interactions. All hydrogen atoms except those participating in the C–H···O hydrogen bonds were omitted for clarity. Symmetry code: ii: *x*, 2 – *y*, –1/2 + *z*. (c) 3D supramolecular frameworks of **4** formed by π – π interactions and C–H···O hydrogen bonds. All hydrogen atoms except those participating in the C–H···O hydrogen bonds were omitted for clarity.

molecule and each unit cell of 7 contains two disordered water molecules and two disordered methanol molecules. These

Fig. 5 (a) 1D polymeric chain of **5**. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–N(1) 2.018(6), Co(1)–N(3) 2.005(6), Co(1)–O(1) 2.155(9), Co(1)–O(2) 2.306(8); N(1)–Co(1)–N(3) 105.6(2), N(1)–Co(1)–O(1) 88.7(3), N(1)–Co(1)–O(2) 140.3(3), N(1)–Co(1)–O(4) 90.8(3), N(1)–Co(1)–O(5) 117.2(3), N(3)–Co(1)–O(5) 86.4(3), O(1)–Co(1)–O(2) 53.3(3), O(1)–Co(1)–O(4) 87.0(4). (b) 2D supramolecular layer of **5** constructed *via* interchain π - π interactions. All hydrogen atoms were omitted for clarity. (c) 3D supramolecular frameworks of **5** formed by π - π interactions and C–H···O hydrogen bonds. All hydrogen atoms except those participating in the C–H···O hydrogen bonds were omitted for clarity. Symmetry code: i: *x*, 1/2 - y, 1/2 + z.

disordered molecules have been treated as a diffuse contribution to the overall scattering without specific atom positions by squeeze.

In complex 8, the coordination polyhedron of the heptacoordinated Cd(n) center can be regarded as a distorted pentagonal bipyramid, where the Cd(n) atom is coordinated by two

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Fig. 6 (a) 1D polymeric chain of **6**. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)-O(1) 1.944(3), Zn(1)-O(4) 1.959(3), Zn(1)-N(1) 2.040(3), Zn(1)-N(3) 2.021(3); N(1)-Zn(1)-N(3) 103.1(1), O(1)-Zn(1)-O(4) 113.4(9), O(1)-Zn(1)-N(1) 106.1(5), O(1)-Zn(1)-N(3) 119.1(7), O(4)-Zn(1)-N(1) 102.5(4), O(4)-Zn(1)-N(3) 110.3(2). (b) 2D supramolecular layer of **6** formed *via* π - π interactions. All hydrogen atoms were omitted for clarity. (c) 3D supramolecular frameworks of **6** formed by π - π interactions and C-H···O hydrogen bonds. All hydrogen atoms except those participating in the C-H···O hydrogen bonds were omitted for clarity. Symmetry code: i: 1 - x, 2 - y, 2 - z.

nitrogen donors from the benzimidazole rings and five oxygen donors (four oxygen donors are from two nitrate groups and the fifth is from DMF). In the hepta-coordinated CdO₅N₂ skeleton, the pentagonal plane for Cd(II) is composed of O(1), O(2), O(4), O(1A) and O(2A) and the axial positions are occupied by N(1) and N(1A) with axial distances of 4.552(8) Å. The axial position is slightly distorted with a N(1)-Cd(1)-N(1A) angle of 174.5(7)°. The degree of pentagonal bipyramid distortion is also reflected in the angles around the Cd(II) atom in the equatorial plane (a regular pentagon value being 72°). In the heptacoordinated Cd(II) environment, the distances of Cd-O vary from 2.322(4) Å to 2.459(2) Å. The Cd(1)-N(1) distance is 2.279(2) Å. The bond angles of N-Cd-O range from 82.0(9)° to $92.5(1)^{\circ}$ and the O-Cd-O bond angles range from $51.9(2)^{\circ}$ to 172.4(0)°. These values are favorably comparable with analogous values from Cd(II) complexes.³⁵



(b)

Fig. 7 (a) 1D polymeric chain of **7**. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): 2n(1)-O(1) 1.963(5), 2n(1)-O(3) 1.926(5), Zn(1)-N(1) 2.005(7), Zn(1)-N(3) 2.017(6); N(1)-Zn(1)-N(3) 111.6(8), O(1)-Zn(1)-O(3) 110.0(9), O(1)-Zn(1)-N(1) 108.9(4), O(1)-Zn(1)-N(3) 96.2(0), O(3)-Zn(1)-N(1) 116.3(9). (b) 2D supramolecular layer of **7** constructed *via* interchain π - π interactions and C-H···O hydrogen bonds. All hydrogen atoms except those participating in the C-H···O hydrogen bonds were omitted for clarity. Symmetry code: i: 2 - x, 1 - y, 1 - z.

The crystal packings of complexes 1-8

In the crystal packing of **1** (Fig. 1(b)), 2D network layers are further extended into 3D supramolecular frameworks by O–H…O hydrogen bonds³⁶ with the help of two free H₂O molecules as bridges (the data of the hydrogen bonds is given in Table 1). In the hydrogen bonds, the hydrogen atoms and oxygen atoms are from coordinated H₂O molecules and free H₂O molecules.

In the crystal packing of 2 (Fig. 2(b)), 2D network layers are further extended into 3D supramolecular frameworks by C–H…O hydrogen bonds³⁷ (Table 1). In the hydrogen bonds, the hydrogen atoms are from imidazole rings and the oxygen atoms are from nitrate groups.

In the crystal packing of 3 (Fig. 3(b)), 2D network layers can be extended into a 3D supramolecular framework $\nu ia \pi - \pi$ stacking interactions³⁸ from the benzene rings of terephthalates



Fig. 8 (a) 1D polymeric chain of **8**. All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Cd(1)–N(1) 2.279(2), Cd(1)–O(1) 2.414(2), Cd(1)–O(2) 2.459(2), Cd(1)–O(4) 2.322(4); N(1)–Cd(1)–N(1A)¹ 174.5(7), N(1)–Cd(1)–O(1) 84.0(3), N(1)–Cd(1)–O(2) 86.6(4), O(1)–Cd(1)–O(2) 51.9(2), O(1)–Cd(1)–O(4) 141.8(2). Symmetry code: i: –*x*, *y*, 1/2 – *z*. (b) 2D supramolecular layer of **8** formed *via* π – π interactions. All hydrogen atoms were omitted for clarity. (c) 3D supramolecular frameworks of **6** formed *via* π – π interactions and C–H···O hydrogen bonds. All hydrogen atoms except those participating in the C–H···O hydrogen bonds were omitted for clarity. Symmetry code: ii: 1/2 - x, 1/2 - y, 1 - z.

and benzimidazole rings (the data of the π - π interactions is given in Table 2).

As shown in Fig. 4(b), 2D supramolecular layers of 4 are formed by 20-membered macrometallocycles *via* intermolecular C–H···O hydrogen bonds (Table 1). In the hydrogen bonds, the hydrogen atoms are from CH₂ groups of alkyl chains and the oxygen atoms are from acetate groups. The 2D supramolecular layers are further extended into 3D supramolecular architectures *via* π – π stacking interactions from the benzimidazole rings, as shown in Fig. 4(c) (Table 2).

In the crystal packings of 5 and 6 (Fig. 5(b) and 6(b)), 1D polymeric chains are extended into 2D supramolecular layers

Table 2 Distances (Å) of the π - π interactions for **3–8**

	π – π		
Compounds	Face-to-face	Center-to-center	
3	3.455(5)	3.867(5)	
4	3.597(1)	3.630(2)	
5	3.403(2)	3.605(1)	
6	3.454(2)	3.856(2)	
7	3.453(4)	3.633(1)	
8	3.496(4)	3.704(4)	

through π - π stacking interactions from the benzimidazole rings (Table 2). The 2D supramolecular layers are further extended into 3D supramolecular architectures *via* C-H···O hydrogen bonds, as shown in Fig. 5(c) and 6(c) (Table 1). In the hydrogen bonds, the hydrogen atoms are from the imidazole rings and the oxygen atoms are from the nitrate groups.

In the crystal packing of 7 (Fig. 7(b)), 2D supramolecular layer is formed through π - π stacking interactions from benzimidazole rings (Table 2) and C-H···O hydrogen bonds (Table 1). In the hydrogen bonds, the hydrogen atoms are from the CH₂ of alkyl chains, and oxygen atoms are from acetate groups.

In the crystal packing of **8** (Fig. 8(b)), 1D polymeric chains are extended into 2D supramolecular layers *via* π - π stacking interactions (Table 2). The 2D supramolecular layers are further extended into 3D supramolecular architectures *via* C-H···O hydrogen bonds, as shown in Fig. 8(c) (Table 1). In the hydrogen bonds, the hydrogen atoms are from the imidazole rings and the oxygen atoms are from nitrate groups.

Compared with the diimidazolyl bidentate ligands, the main feature of dibenzimidazolyl bidentate ligands is that the benzimidazole ring is easer to participate in π - π interactions between molecules due to a large conjugated system. The π - π interactions between the benzimidazole rings generally include three types (Scheme 1), namely, a head-to-tail type (such as complexes 5–7 and the $Co(\pi)$ complexes reported²⁸), a tail-to-tail type (like complex 4) and a shoulder-to-shoulder type (like complex 8). These different overlaps may be related to the metal atoms connected to the benzimidazole rings and the steric hindrance around the benzimidazole rings. Furthermore, the benzimidazole ring and other π systems (like benzene rings) can also form π - π interactions (such as complex 3 and the Ni(II) complexes reported²⁹). These π - π interactions along with other weak interactions (like hydrogen bonds) can provide more opportunities for constructing supramolecular architectures. Additionally, the π - π stacking



Scheme 1 The π - π interactions from the benzimidazole ring.

interactions are also helpful in stabilizing the supramolecular architectures.

The conformations of the bidentate ligands (bibim-*m* or biim-*m*) and their metal complexes

According to literature reports and our results obtained here, the dibenzimidazolyl (or diimidazolyl) bidentate ligands with alkanyl linkers (**bibim-m** or **biim-m**, bibim = 1,*m*-bis(benzimidazol-l-yl)alkane, biim = 1,*m*-bis(imidazol-l-yl)alkane, m = 1-6) can rotate and bend freely around the $-(CH_2)_m$ - linkers when coordinating to the central metal atoms. These bidentate ligands contain mainly three types of conformations, namely, *cis-*, *trans-* and *gauche-*conformations, as shown in Scheme 2. In the different conformations, the dihedral angles between two benzimidazole (or imidazole) rings are different.

The metal complexes formed *via* bidentate ligands (**bibim***m* or **biim***m*) and metal salts contain mainly five types of conformations (Scheme 3): (1) 1D single-stranded polymeric



Scheme 2 The conformations of the dibenzimidazolyl (or diimidazolyl) bidentate ligands with alkanyl linkers.

chains (I) formed by the bidentate ligands and metal atoms (such as complexes 5-8, {[Ag(biim-1)](ClO₄)}_n,¹⁷ [Zn(bibim-1)-(hba)]_n (hba = p-hydroxybenzoate)¹⁸ and $[Zn(biim-6)Cl_2]_n^{19}$), in which the 1D polymeric chain adopts a zig-zag coordination geometry. (2) 1D double-stranded polymeric chains (II) formed by bidentate ligands and metal atoms (such as {[Cu(biim-1)₂- $(H_2O)_2](Cl)_2\}_n$,¹⁷ {[(Cu(biim-1)_2(OH)](Cl)]_n and [Cu(biim-1)_2- $(NO_3)_2]_n^{20}$ and $[Co(biim-5)_2(H_2O)_2]_n^{21}$, in which the monomer of the polymeric chain is a macrometallocycle and each macrometallocycle is formed by two bidentate ligands and two metal atoms. Among the coordinating atoms of each metal center, four of them are nitrogen donors from four different dibenzimidazolyl (or diimidazolyl) bidentate ligands and the other coordinating atoms are from counter-ions or solvent molecules. (3) The metallomacrocycle (III) formed by two bidentate ligands and two metal atoms (such as complex 4 and $[Cd_2(biim-1)_2(HL)_4)]$ (H₂L = 3-methylsalicylic acid)²²), in which the metallomacrocycle is similar to the above-mentioned macrometallocycle monomer of II. However, among the coordinating atoms of each metal center in III, two of them are nitrogen donors from two different dibenzimidazolyl (or diimidazolyl) bidentate ligands and the other coordinating atoms are from counter-ions, solvent molecules or single functional group ligands (such as acetate, p-methylbenzoate and *p*-bromobenzoate). Therefore, this case can form only single metallomacrocycles. (4) 2D layers with the metallomacrocycles (IV) (such as complexes 1 and 2, $\{[Cu(biim-1)_2](BF_4)_2\}_n^{17}$ and $[Fe(biim-2)_2(N_3)_2]_n^{23})$, in which each metallomacrocycle



Scheme 3 The conformations formed by the dibenzimidazolyl (or diimidazolyl) bidentate ligands and metal salts.

monomer is constructed *via* four dibenzimidazolyl (or diimidazolyl) bidentate ligands and four metal atoms. (5) 3D frameworks (**V**) formed by dibenzimidazolyl (or diimidazolyl) bidentate ligands and metal atoms (such as $\{[Ni(biim-4)_3]-(NO_3)_2\}_n^{24}$ and $\{[Zn(biim-1)_3](ClO_4)_2\}_n^{17}$), in which each metal atom is coordinated to six nitrogen donors from six different bidentate ligands. When the dibenzimidazolyl (or diimidazolyl) bidentate ligands with alkanyl linkers and other compounds (like organic diacids) as mixed ligands are coordinated to metal atoms, distinct dimensionality and connectivity of the complexes can also be afforded (such as complex 3 and other complexes reported²⁵⁻²⁷).

Additionally, the influence of metal ions on the conformations of metal complexes can also not be ignored. Different transition metal ions have different electronic structure characteristics. In the course of preparing metal complexes, when the metal ion is different and ligand is the same, the structure of the complexes obtained may be different or similar. For example, the Co(II) complex 1 and Zn(II) complex 6 contain different metal ions and the same bibim-4 ligand and they have different conformations (the former is a 2D network layer and the latter is a 1D polymeric chain (Fig. 1(a) and 6(a))). In contrast, the Co(II) complex 1 and Cu(II) complex 2 also contain different metal ions and the same bibim-4 ligand, but they have similar 2D network layers (Fig. 1(a) and 2(a)). Likewise, the Zn(II) complex 6 and Cd(II) complex 8 contain different metal ions and the same bibim-4 ligand and they have similar 1D polymeric chains (Fig. 6(a) and 8(a)). It is notable that the same metal ion in the complexes may possess a different coordination number, such as the coordination number of Co(II) is 4 for complex 3, 5 for [Co(bibim-4)(glutarate)] $_{n}^{29}$ and 6 for complex 1.

In complexes **6** and **7**, the metal ion and ligand are all the same, only the counter-ions are different, and the two complexes possess similar 1D polymeric chains. This indicates that counter-ions have a relatively small influence on the conformation of complexes. On the whole, the conformations of metal complexes based on the dibenzimidazolyl (or diimidazolyl) bidentate ligands are related mainly to the length of the alkanyl chains, metal ions and counter-ions as well as the steric hindrance around the metal centers.

IR spectra analysis of 1-8

complexes 1-8, the absorption In bands around 3000–2800 cm⁻¹ can be assigned to aromatic ν (C-H) modes. The bands in the region of 1653–1515 cm⁻¹ may be ascribed to C–H bending vibrations. the The bands around 1619–1609 cm⁻¹ may result from ν (C=N) of the benzimidazole rings. The bands in the 1265-1200 cm⁻¹ region may result from $\nu_{s}(C-C)$ or $\nu_{s}(C-N)$ of the benzene rings or imidazole rings. These values are similar to those of the ligands (bibim*m*, m = 2-4). The strong absorption bands about 1395 cm⁻¹ originate from ν (C–O) of the acetate groups for 4 and 7. The strong bands at 3448 cm⁻¹ for **1** should be ascribed to ν (O–H) of coordinated water molecules. The strong bands at 1594–1652 cm⁻¹ for 3, 4, 7 and 8 correspond to ν (C=O) of



Fig. 9 Emission spectra of the ligands (**bibim-**m, m = 2-4) and complexes **1–8** at room temperature in a CH₃CN (5.0 × 10⁻⁶ M) solution.

terephthalate or DMF. The middle absorption bands at 1378–1395 cm⁻¹ for **2**, **5**, **6** and **8** correspond to ν (N–O) of the nitrate groups.

Fluorescence emission spectra of the ligands (bibim-*m*) and complexes 1–8

As indicated in Fig. 9, the fluorescence emission spectra of the ligands (**bibim-***m*, m = 2-4), and complexes **1–8** in acetonitrile at room temperature are obtained upon excitation at 240 nm. These ligands (**bibim-***m*) have similar fluorescence emission spectra and they show weak double emission bands centered at 305 nm and 335 nm, corresponding to intraligand transitions.³⁹ The fluorescence emission of complexes **1–8** are similar to those of the ligands (**bibim-***m*), which should originate from metal perturbed intraligand processes.⁴⁰ In complexes **1–8**, a new peak at about 280–285 nm is observed and it may be ascribed to the incorporation of metal–ligand coordination interactions.⁴¹

Conclusions

Among eight Co(II), Zn(II), Cu(II) and Cd(II) complexes based on dibenzimidazolyl bidentate ligands with alkyl linkers, seven complexes, **1**, **2** and **4–8**, were prepared by an analogous method *via* the reaction of the corresponding ligands with the metal salts in CH₃OH–DMF (the molar ratio between the ligand and metal salt being 1:2). But the method of preparation of complex **3** was somewhat different from the abovementioned method. In the preparation of complex **3**, although **bibim-3** and Co(NO₃)₂·6H₂O (1:2) were added, 1 equivalent of terephthalic acid was also used in the presence of Et₃N. As a result, the terephthalate group together with **bibim-3** participate in the coordination with the Co(II) atoms to afford 2D network layers with macrometallocycles.

In complexes 1 and 2, 2D network layers with macrometallocycles are formed *via* the **bibim-4** ligand and Co(II) or Cu(II)atoms. In complex 4, a 20-membered macrometallocycle is formed by two bibim-3 ligands and two Zn(II) atoms. In complexes 5-8, 1D polymeric chains are formed via the bibim-2 or **bibim-4** ligands and $Co(\pi)$, $Zn(\pi)$ or $Cd(\pi)$ centers. The dibenzimidazolyl (or diimidazolyl) bidentate ligands (bibim-m or biim-m) with alkanyl linkers contain mainly three types of conformations (i.e. cis-, trans- and gauche-conformations) and their complexes contain mainly five types of conformations (i.e. 1D single-stranded polymeric chains, 1D double-stranded polymeric chains, the metallomacrocycle, 2D layers with the metallomacrocycles and 3D frameworks). In the crystal packings of complexes 1-8, 2D supramolecular layers or 3D supramolecular frameworks are formed via intermolecular weak interactions, including π - π interactions and hydrogen bonds. The coordination of dibenzimidazolyl bidentate ligands bearing alkanyl linkers with metal atoms is similar to the case of diimidazolyl bidentate ligands. The main difference of the dibenzimidazolyl bidentate ligands and diimidazolyl bidentate ligands is that the conjugated system of the benzimidazole ring is bigger than that of the imidazole ring and the benzimidazole ring participates more easily in π - π interactions between molecules. Therefore, the complexes based on dibenzimidazolyl bidentate ligands can form more varied architectures via π - π interactions and other weak interactions (like hydrogen bonds). The resultant structures of the complexes will provide valuable experimental data for crystal engineering and supramolecular chemistry. Additionally, the macrocyclic structures of these metal complexes suggest that they may have potential applications in host-guest chemistry. Further studies on new organometallic compounds from the precursors and analogous ligands are underway.

Experimental

General procedures

The **bibim-***m* ligands (m = 2, 3 and 4) were prepared with analogous methods to the literature.⁴² All the reagents for the synthesis and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ¹H NMR spectra were recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts, δ , are reported in ppm relative to the internal standard TMS for both ¹H NMR and *J* values are given in Hz. The elemental analyses of all compounds were obtained from the recrystallised powder compounds and measured using a Perkin-Elmer 2400C Elemental Analyzer. IR spectra (KBr) were taken on an Bruker Equinox 55 spectrometer. The luminescent spectra were conducted on a Cary eclipse fluorescence spectrophotometer.

Preparation of 1,2-bis(benzimidazol-l-yl)ethane (bibim-2)

Benzimidazole (1.300 g, 11.0 mmol) and CH_3CN (100 mL) were added to a flask fitted with a condenser and stirred for 15 min

at ambient temperature. Then KOH (0.925 g, 16.5 mmol) and tetrabutylammonium bromide (0.106 g, 33.3 mmol) were added. After the mixture was stirred for 2 h under refluxing, 1,2-dibromoethane (0.939 g, 5.0 mmol) was slowly added through a syringe and stirred continually for 24 h at 80 °C. The reaction was stopped and the solvent was removed under vacuum to afford a yellow oil. The yellow oil was dissolved in CH_2Cl_2 (100 mL) and washed with water (100 mL \times 3) and the organic layer was dried over anhydrous MgSO₄. After filtering, the filtrate was evaporated to give the crude product and the product was further purified by recrystallization from methanol-diethyl ether to give 1,2-bis(benzimidazol-l-yl)ethane as a white powder (bibim-2). Yield: 0.590 g (45%). M.p.: 240–242 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 4.72 (s, 4H, CH₂), 7.16 (m, 4H, PhH), 7.38 (d, J = 4.8, 2H, PhH), 7.58 (d, J = 4.8, 2H, PhH), 7.89 (s, 2H, 2-imiH). Anal. Calc. for C₁₆H₁₄N₄: C, 73.26; H, 5.37; N, 21.36%. Found: C, 73.53; H, 5.44; N, 21.51%. IR (KBr, cm⁻¹): 2963w, 1606w, 1490s, 1461s, 1410w, 1370m, 1334m, 1289w, 1266s, 1204m, 1167s, 1001w, 941w, 881m, 770m, 756vs, 628m, 583w.

The ligands 1,3-bis(benzimidazol-l-yl)propane (**bibim-3**) and 1,4-bis(benzimidazol-l-yl)butane (**bibim-4**) were prepared in a manner analogous to that of **bibim-2**, only with 1,3-dibromopropane or 1,4-dibromobutane instead of 1,2-dibromoethane.

Preparation of 1,3-bis(benzimidazol-l-yl)propane (bibim-3)

Yield: 1.075 g (79%). M.p.: 152–154 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 2.49 (m, 2H, CH₂), 4.30 (s, 4H, NCH₂), 7.22 (m, 4H, PhH), 7.55–7.65 (m, 4H, PhH), 8.25 (s, 2H, 2-imiH). Anal. Calc. for C₁₇H₁₆N₄: C, 73.89; H, 5.84; N, 20.27%. Found: C, 73.63; H, 5.96; N, 20.57%. IR (KBr, cm⁻¹): 2925w, 1731w, 1611m, 1478s, 1449s, 1387m, 1370m, 1334w, 1283s, 1225s, 1200w, 1143w, 1055m, 1001m, 925w, 889w, 871m, 740vs, 631w, 416m.

Preparation of 1,4-bis(benzimidazol-l-yl)butane (bibim-4)

Yield: 0.975 g (73%). M.p.: 174–175 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 1.78 (m, 4H, CH₂), 4.27 (s, 4H, NCH₂), 7.23 (m, 4H, PhH), 7.57–7.66 (m, 4H, PhH), 8.22 (s, 2H, 2-imiH). Anal. Calc. for C₁₈H₁₈N₄: C, 74.46; H, 6.25; N, 19.30%. Found: C, 74.54; H, 6.65; N, 19.43%. IR (KBr, cm⁻¹): 2929m, 2855m, 1752w, 1606m, 1499vs, 1459s, 1436s, 1378s, 1281s, 1250s, 1154m, 1160m, 1009m, 925w, 889w, 876m, 740vs, 640m.

Preparation of $\{ [Co(bibim-4)_2(H_2O)_2](NO_3)_2 \}_n (1)$

A DMF solution (5 mL) containing **bibim-4** (0.100 g, 0.3 mmol) was added to a methanol solution (15 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.175 g, 0.6 mmol). The reaction mixture was stirred for 30 min at about 40 °C. Then the reaction mixture was filtered and the filtrate was left to stand at room temperature. Purple block crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents within seven days. Yield: 99.1 mg (59%) (based on **bibim-4**). M.p.: 318–319 °C. Anal. Calc. for $C_{36}H_{40}CoN_{10}O_8$: C, 46.96; H, 6.22; N, 14.41%. Found: C, 47.14; H, 6.56; N, 14.64%. IR (KBr, cm⁻¹): 3440s, 2934w, 2884w,

2361w, 2025w, 2017w, 1652m, 1615m, 1515s, 1461s, 1387vs, 1333vs, 1257s, 1204m, 1009w, 926w, 893w, 827w, 760s, 740s, 449w, 429w.

Preparation of $\{[Cu(bibim-4)_2(NO_3)](NO_3)\}_n$ (2)

This complex was prepared in a manner analogous to that of **1** only using Cu(NO₃)₂·6H₂O (0.145 g, 0.6 mmol) instead of Co (NO₃)₂·6H₂O and blue block single crystals of **2** suitable for X-ray analysis were obtained within two weeks. Yield: 77.8 mg (57%) (based on bibim-4). M.p.: 294–296 °C. Anal. Calc. for C₃₆H₃₆CuN₁₀O₆: C, 56.28; H, 4.72; N, 18.23%. Found: C, 56.54; H, 4.53; N, 18.43%. IR (KBr, cm⁻¹): 2950w, 2353w, 2025m, 1615m, 1515s, 1467m, 1395s, 1316s, 1287s, 1262m, 1196m, 1045w, 1009w, 929w, 867w, 772m, 748s, 653w, 618m.

Preparation of $[Co(bibim-3)(TP)]_n$ (3)

A DMF solution (5 mL) containing terephthalic acid (0.066 g, 0.4 mmol) and **bibim-3** (0.100 g, 0.4 mmol) was added to a methanol solution (15 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.233 g, 0.8 mmol) and the pH value of the solution was adjusted to approximately 7 by triethylamine. The reaction mixture was stirred for 30 min at about 40 °C. Then the reaction mixture was filtered and the filtrate was left to stand at room temperature. Purple crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents within seven days. Yield: 0.120 g (53%) (based on **bibim-3**). M.p.: >320 °C. Anal. Calc. for $C_{50}H_{40}Co_2N_8O_8$: C, 60.13; H, 4.04; N, 11.22%. Found: C, 60.43; H, 4.32; N, 11.46%. IR (KBr, cm⁻¹): 2952w, 2357w, 2025w, 1602m, 1582s, 1503m, 1391s, 1291w, 1258w, 1196w, 1013w, 916w, 824w, 740s, 520w, 425w.

Preparation of $[Zn_2(bibim-3)]_2(OAc)_4](4)$

This complex was prepared in a manner analogous to that of 1 only **bibim-3** (0.100 g, 0.4 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (0.176 g, 0.8 mmol) was used instead of **bibim-4** and $Co(NO_3)_2 \cdot 6H_2O$. Colorless single crystals of 4 suitable for X-ray analysis were obtained within two weeks. Yield: 0.105 g (57%) (based on **bibim-3**). M.p.: 120–122 °C. Anal. Calc. for $C_{21}H_{22}N_4ZnO_4$: C, 54.85; H, 4.82; N, 12.18%. Found: C, 54.84; H, 4.63; N, 12.42%. IR (KBr, cm⁻¹): 2971w, 2921w, 1615vs, 1586s, 1515m, 1395s, 1337m, 1200m, 922m, 744s, 675m, 618w, 498w, 428w.

Preparation of $[Co(bibim-2)(NO_3)_2]_n$ (5)

This complex was prepared in a manner analogous to that of **1**, and only **bibim-2** (0.105 g, 0.4 mmol) was used instead of **bibim-4**. Pink single crystals of 5 suitable for X-ray analysis were obtained within two weeks. Yield: 0.105 g (62%) (based on **bibim-2**). M.p.: 358–360 °C. Anal. Calc. for $C_{16}H_{14}CON_6O_6$: C, 43.16; H, 3.17; N, 18.87%. Found: C, 43.44; H, 3.51; N, 18.64%. IR (KBr, cm⁻¹): 2961w, 2021w, 1615w, 1490vs, 1461s, 1382s, 1287vs, 1204m, 1009m, 922m, 810m, 744s, 628w, 420m.

Preparation of $[Zn(bibim-4)(NO_3)_2]_n$ (6)

This complex was prepared in a manner analogous to that of **1** only using $Zn(OAc)_2 \cdot 2H_2O$ (0.176 g, 0.8 mmol) instead of Co $(NO_3)_2 \cdot 6H_2O$. Colorless single crystals of **6** suitable for X-ray

analysis were obtained within two weeks. Yield: 0.102 g (62%) (based on **bibim**-4). M.p.: 258–260 °C. Anal. Calc. for $C_{18}H_{18}ZnN_6O_6$: C, 45.06; H, 3.78; N, 17.52%. Found: C, 45.33; H, 3.86; N, 17.83%. IR (KBr, cm⁻¹): 2946w, 2871w, 2370w, 2029w, 1619m, 1582s, 1548s, 1520s, 1461s, 1378vs, 1329s, 1295s, 1258m, 1201w, 1009w, 939w, 925w, 756s, 738s, 672m, 618m, 498m, 422m.

Preparation of $[Zn(bibim-4)(OAc)_2]_n$ (7)

This complex was prepared in a manner analogous to that of **1** only $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.176 g, 0.8 mmol) was used instead of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Colorless single crystals of 7 suitable for X-ray analysis were obtained within two weeks. Yield: 0.110 g (59%) (based on **bibim**-4). M.p.: 274–276 °C. Anal. Calc. for $\text{C}_{22}\text{H}_{24}\text{ZnN}_4\text{O}_4$: C, 55.76; H, 5.11; N, 11.82%. Found: C, 55.73; H, 5.36; N, 11.65%. IR (KBr, cm⁻¹): 2950w, 2926w, 2356w, 2328w, 2025w, 1594vs, 1523s, 1470m, 1391vs, 1333m, 1299m, 1258m, 1225m, 1196m, 1171m, 1005m, 925m, 751s, 678m, 621w, 431m.

Preparation of [Cd(bibim-4)(NO₃)₂(DMF)]_n (8)

This complex was prepared in a manner analogous to that of **1**, and only $Cd(NO_3)_2 \cdot 4H_2O$ (0.185 g, 0.6 mmol) was used instead of $Co(NO_3)_2 \cdot 6H_2O$ and colorless needle-like single crystals of **8** suitable for X-ray analysis were obtained within two weeks. Yield: 0.126 g (61%) (based on **bibim-4**), M.p.: 340–342 °C. Anal. Calc. for $C_{21}H_{25}CdN_7O_7$: C, 42.05; H, 4.20; N, 16.34%. Found: C, 42.42; H, 4.41; N, 16.53%. IR (KBr, cm⁻¹): 2963m, 2938m, 2880w, 2365w, 2029w, 1652m, 1615m, 1523s, 1465s, 1382vs, 1333vs, 1295s, 1225s, 1014w, 918m, 876m, 823m, 752s, 618m, 511m, 422m.

X-ray data collection and structure determinations

X-ray single-crystal diffraction data for complexes 1-8 were collected using a Bruker Apex II CCD diffractometer at 296(2) K with Mo–K α radiation (λ = 0.71073 M) using the ω scan mode. There was no evidence of crystal decay during the data collection in all cases. Semiempirical absorption corrections were applied using SADABS and the program SAINT was used for the integration of the diffraction profiles.⁴³ All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL⁴⁴ by the fullmatrix least-squares method, with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . Hydrogen atoms bonded to C atoms were placed geometrically and presumably solvent H atoms were first located in difference Fourier maps and then fixed in the calculated sites. Further details for the crystallographic data and structural analysis are listed in Tables 3-5, generated using Crystal-Maker.45

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Table 3 Crystal data and structure refinements for 1–3

	1	2	3
Chemical formula	C ₃₆ H ₄₂ CoN ₁₀ O ₁₀ ·3H ₂ O·MeOH	$C_{72}H_{72}Cu_2N_{20}O_{14}\cdot H_2O$	C ₅₀ H ₄₀ Co ₂ N ₈ O ₈ ·2DMF·2CH ₃ COCH ₃
fw	919.82	1586.59	1261.11
Cryst syst	Monoclinic	Orthorhombic	Triclinic
Space group	P_2/n	$Pna2_1$	$P\bar{1}$
a/Å	15.226(3)	14.090(0)	9.968(3)
b/Å	9.601(5)	16.386(2)	11.420(2)
C/Å	16.916(3)	16.393(2)	14.055(2)
$\alpha / ^{\circ}$	90	90	74.5(9)
$\beta/^{\circ}$	97.8(6)	90	82.3(7)
$\gamma/^{\circ}$	90	90	83.5(6)
$V/Å^3$	2449.7(7)	3784.8(8)	1524.0(4)
Ζ	2	2	1
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	1.247	1.392	1.374
Abs coeff/mm ⁻¹	0.418	0.640	0.614
F(000)	966	1648	658
Cryst size/mm	0.28 imes 0.22 imes 0.20	0.23 imes 0.20 imes 0.18	0.23 imes 0.22 imes 0.12
$\theta_{\min}, \theta_{\max}/^{\circ}$	2.43, 24.74	1.76, 25.01	2.07, 25.03
T/K	296(2)	296(2)	296(2)
No. of data collected	12 138	18 511	6398
No. of unique data	4329	5458	5243
No. of refined params	295	500	392
Goodness-of-fit on F^{2a}	1.095	1.060	1.074
Final R indices ^b $[I > 2\sigma(I)]$			
R_1	0.0734	0.0533	0.1002
wR_2	0.2412	0.1451	0.2311
R indices (all data)			
R_1	0.0878	0.0587	0.1708
wR ₂	0.2558	0.1507	0.2640

^{*a*} Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. ^{*b*} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

 Table 4
 Crystal data and structure refinements for 4–6

	4	5	6
Chemical formula	C42H44N8Zn2O8.2EtOH	C ₁₆ H ₁₄ CoN ₆ O ₆	C ₁₈ H ₁₈ NZn ₆ O ₆ ·0.25H ₂ O
fw	1011.73	445.26	484.26
Cryst syst	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$
a/Å	23.392(8)	15.631(1)	9.409(3)
b/Å	9.347(2)	7.591(5)	16.653(5)
c/Å	22.029(9)	14.592(9)	14.836(1)
$\alpha / ^{\circ}$	90	90	90
$\beta / ^{\circ}$	94.4(0)	93.0(4)	101.1(3)
γ/°	90	90	90
$V/Å^3$	4802.8(5)	1729.0(1)	2281.0(3)
Ζ	4	4	4
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	1.399	1.710	1.410
Abs coeff/mm ⁻¹	1.063	1.045	1.122
F(000)	2112	908	994
Cryst size/mm	0.22 imes 0.20 imes 0.16	$0.38 \times 0.36 \times 0.20$	0.36 imes 0.32 imes 0.26
$\theta_{\rm min}, \theta_{\rm max}/^{\circ}$	1.75, 25.03	1.30, 25.03	1.86, 25.03
T/K	296(2)	296(2)	296(2)
No. of data collected	11 996	8250	11 513
No. of unique data	4239	3047	4025
No. of refined params	327	262	280
Goodness-of-fit on F^{2a}	1.020	1.019	1.014
Final <i>R</i> indices ^{<i>b</i>} $[I > 2\sigma(I)]$			
R ₁	0.0332	0.0754	0.0539
wR_2	0.0804	0.1981	0.1766
R indices (all data)			
R ₁	0.0522	0.1122	0.0604
wR_2	0.0888	0.2363	0.1821

^{*a*} Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. ^{*b*} $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 5 Crystal data and structure refinements for 7 and 8

	7	8
Chemical formula	C ₂₆ H ₃₇ N ₅ O ₇ Zn	C ₂₁ H ₂₅ CdN ₇ O ₇
fw	596.98	599.88
Cryst syst	Triclinic	Monoclinic
Space group	P_1	C2/c
a/Å	8.951(8)	17.857(4)
b/Å	10.837(4)	9.759(3)
c/Å	14.050(5)	14.519(2)
$\alpha / ^{\circ}$	76.6(4)	90
$\beta/^{\circ}$	76.3(0)	102.2(1)
γ/°	79.0(9)	90
$V/Å^3$	1275.4(3)	2473.0(8)
Ζ	2	4
$D_{\rm calcd}/{\rm Mg}~{\rm m}^{-3}$	1.554	1.611
Abs $coeff/mm^{-1}$	1.020	0.938
F(000)	628	1216
Cryst size/mm	0.28 imes 0.26 imes 0.22	0.25 imes 0.23 imes 0.20
$\theta_{\min}, \theta_{\max}/^{\circ}$	1.95, 25.02	2.39, 25.01
T/K	296(2)	296(2)
No. of data collected	6537	6016
No. of unique data	4459	2176
No. of refined params	282	188
Goodness-of-fit on F^{2a}	1.076	1.090
Final <i>R</i> indices ^{<i>b</i>} $[I > 2\sigma(I)]$		
R ₁	0.0323	0.0243
wR_2	0.0883	0.0621
R indices (all data)		
R ₁	0.0368	0.0265
wR_2	0.0905	0.0640

^{*a*} Goof = $[\Sigma \omega (F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined. ^{*b*} $R_1 = \Sigma(||F_o| - |F_c||) / \Sigma |F_o|$; $wR_2 = 1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

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