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Hydrothermal syntheses, coordination isomerism and UV-VIS absorption of Co^{II} and Ni^{II} complexes with mixed ligands

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The new complexes $\{[Co_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ and $\{[Ni_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ have been synthesized under solvothermal conditions. These isostructural complexes exhibit 2D bilayer networks with unprecedented $\{4^{11}.6^4\}$ topology.

The construction of coordination polymers with new topology has been of intense interest due to their intriguing aesthetic structures and use in the crystal engineering.[1–4] The most new topology types of coordination polymers described recently are three-dimensional, while completely new 2D topology types have been barely reported.[4,5] Moreover, coordination polymers based on N-containing ligands attracted attention due to their novel architectures and special properties.[6–8] Pyridyl ligands, which possess excellent coordination ability to meet the requirement of coordination geometries of metal ions, have been widely used in the construction of coordination polymers.[9–11] Therefore, the design and synthesis of new pyridyl ligands are meaningful for the construction of coordination polymers with novel architectures and functions.

Recently, we synthesized a new V-shape ligand, bis[4-(pyridin-4-yl)phenyl]amine (BPPA) by the Suzuki aryl-coupling reaction.[12] Meanwhile, we adopted (hexafluoroisopropylidene)bis-(benzoic acid) (H_2hfipbb)[13] as an achiral co-ligand to react with bivalent metal salts. Here, two new coordination polymers with completely new topology were obtained under solvothermal conditions,[†] namely $\{[Co_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ **1** and $\{[Ni_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ **2**. The complexes were characterized by elemental analysis, IR spectra, X-ray powder diffraction and X-ray crystallography.[‡] A semi-empirical absorption correction was applied using SADABS.[16]

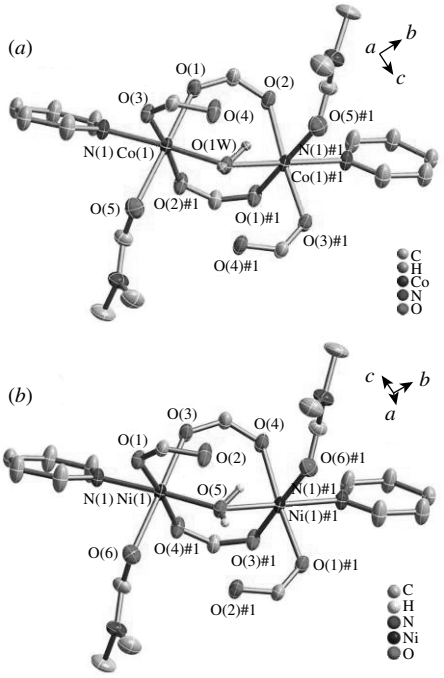

Figure 1 Coordination environments of complexes (*a*) **1** and (*b*) **2** (30% ellipsoid probability). Most hydrogen atoms are omitted for clarity. Symmetry codes for **1**: #1 = *x*, 0.5 – *y*, 0.5 – *z*; for **2**: #1 = *x*, 0.5 – y, 0.5 – *z*. Selected bond lengths (Å) in **1**: Co(1)–O(1) 2.0524(19), Co(1)–O(2)#1 2.0630(19), Co(1)–O(1W) 2.0884(14), Co(1)–O(3) 2.1104(18), Co(1)–N(1) 2.120(2), Co(1)–O(5) 2.224(2). Selected bond lengths (Å) in **2**: Ni(1)–O(3) 2.0228(14), N(1)–Ni(1) 2.0795(16), Ni(1)–O(4)#1 2.0410(14), Ni(1)–O(5) 2.0410(10), Ni(1)–O(1) 2.0900(14), Ni(1)–O(6) 2.1654(15).

† Commercial reagents and solvents were used as received.

Synthesis of complexes **1** *and* **2** *(general procedure).* A mixture of $M(NO_3)_2{\cdot}6H_2O$ (M = Co or Ni, 0.1 mmol), BPPA (32.3 mg, 0.1 mmol) and H_2hfipbb (39 mg, 0.1 mmol) was dissolved in 15 ml of DMF–H_2O (1:1). The mixture was placed in a Parr Teflon-lined stainless steel vessel (25 ml) under autogenous pressure and heated at 95 °C for three days. Crystals were collected (yields based on BPPA ligand: ~86% for **1**, ~80% for **2**).

‡ *Crystallographic data for* **1** *and* **2**.

For **1**: $C_{62}H_{49}Co_2F_{12}N_5O_{11}$, M_r = 1385.92, orthorhombic, space group *Pnna*, *a* = 26.4549(12), *b* = 17.1611(8) and *c* = 15.0516(7) Å, *V* = = 6833.4(5) Å^3, *Z* = 4, d_{calc} = 1.347 g cm^{-3}, μ(MoKα) = 0.576 mm^{-1}, *T* = 296(2) K, 36462 reflections measured, 6038 independent reflections (R_{int} = 0.0276), final R_1 [$I > 2\sigma(I)$] = 0.0432, $wR(F^2)$ = 0.1270, GOF = = 1.040.

For **2**: $C_{62}H_{49}Ni_2F_{12}N_5O_{11}$, M_r = 1385.48, orthorhombic, space group *Pnna*, *a* = 26.5858(18), *b* = 16.9873(11) and *c* = 15.0087(10) Å, *V* = = 6778.2(8) Å^3, *Z* = 4, d_{calc} = 1.358 g cm^{-3}, μ(MoKα) = 0.647 mm^{-1}, *T* = 296(2) K, 36202 reflections measured, 5981 independent reflections (R_{int} = 0.0482), final R_1 [$I > 2\sigma(I)$] = 0.0429, $wR(F^2)$ = 0.1181, GOF = = 1.030.

The measurements were performed on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[14] The restraint DELU (rigid-bond) was applied to restrain the U_{ij} values of atoms with the default esd. (DELU 0.001 C14 O5 Co1 O5). The distributions of peaks in the channels of **1** and **2** were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON.[15] Numbers of solvent water molecules in **1** and **2** were obtained by thermo analyses. Hydrogen atoms positions were fixed geometrically at calculated distances and allowed riding on the parent atoms.

For the topological analysis and producing some diagrams the TOPOS 4.0 program[17] was used. The thermal analysis and UV-VIS absorption data for **1** and **2** are discussed in detail.

The crystal structure determination[14–17] reveals that complex **1** crystallizes in the orthorhombic crystal system *Pnna*. The asymmetric unit of **1** contains two Co^{2+} ions, one BPPA molecule, two $hfipbb^{2-}$ anions, one coordinated water molecule, two DMF molecules and four lattice water molecules. As shown in Figure 1, the O(1W) atom from water molecule coordinated to two Co^{2+} ions, forming a binuclear secondary building unit (SBU) $[Co_2(H_2O)]$ in **1**. The Co(1)–O(1W) bond length is 2.0884(14) Å, and the Co(1)–O(1W)–Co(1)#1 bond angle is 116.81(12)°.

The two Co atoms in the SBU have an octahedral coordination environment with one N atom (from the BPPA molecule) and five O atoms (from one DMF molecule, one water molecule and three carboxyl groups from three $hfipbb^{2-}$ anions). Therefore, each $[Co_2(H_2O)]$ SBU in **1** links four $hfipbb^{2-}$ anions, two BPPA ligands and two DMF molecules. The Co–N bond length is 2.120(2) Å, and the Co–O lengths are 2.052–2.224 Å, which are similar to those in other Co complexes.[18–20] The dihedral angle between pyridyl and adjacent phenyl rings in BPPA molecule is 16.524(93)°.

On the one hand, each of the two adjacent $hfipbb^{2-}$ anions [including O(1) and O(2)] in **1** are linked by neighbouring $[Co_2(H_2O)]$ SBUs, giving rise to window A (Figure 2). In windows A, the adjacent distance of C(23)···$[Co_2(H_2O)]$ is 8.3624(17) Å, and the angle of adjacent $[Co_2(H_2O)]$–C(23)–$[Co_2(H_2O)]$ is 110.068(1)°. On the other hand, the BPPA ligand and the adjacent $hfipbb^{2-}$ anion [including O(3) and O(4)] are connected by $[Co_2(H_2O)]$ SBUs, forming window B (Figure 2). In windows B, the adjacent distances of C(31)···$[Co_2(H_2O)]$ and N(2)···$[Co_2(H_2O)]$ are 9.4595(23) and 12.2470(12) Å, respectively, and the angles of adjacent $[Co_2(H_2O)]$–C(31)–$[Co_2(H_2O)]$ and $[Co_2(H_2O)]$–N(2)–$[Co_2(H_2O)]$ are 105.420° and 137.473°, respectively. These two kinds of windows form a 2D network by sharing the $[Co_2(H_2O)]$ SBUs (Figure 2). A view of the 2D network of **1** along the *a* axis is shown in Figure 3.

Complex **1** contains a small solvent-accessible void space of 15.7% of the total crystal volume calculated by the PLATON program.[15] Recently, 2D coordination networks containing cavities or channels attracted much attention due to their function in finely tuning the shape and size of cavities.[21]

There is no obvious difference between the crystallographic data and coordination modes (Figure 1) of metal atoms in **1** and **2**. Complexes **1** and **2** are isostructural despite of using different metal salts; therefore, we do not discuss the crystal structure of **2**.

A better insight into this intricate network can be accessed by a topological method.[17] Since complexes **1** and **2** are also isostructural from the topological point of view, the topology structure of **1** is described here.

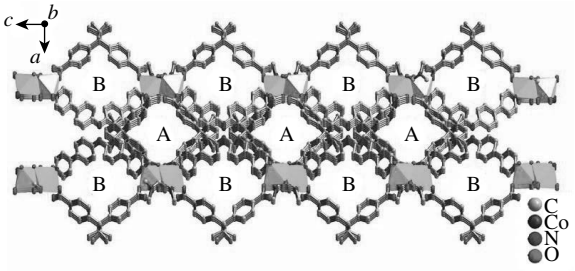

Figure 2 A view of 2D network of **1** along the *b* axis.

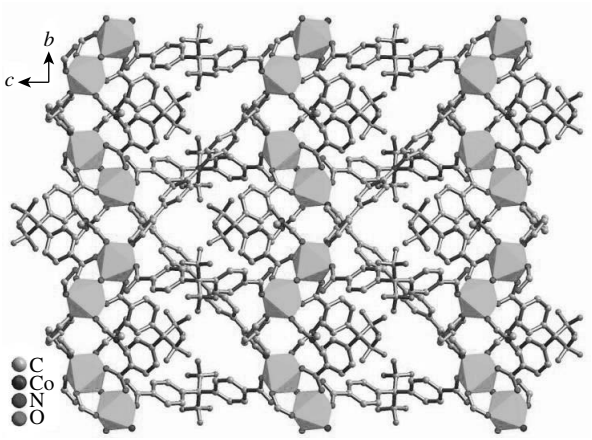

Figure 3 A view of 2D network of **1** along the *a* axis.

In complex **1**, the $[Co_2(H_2O)]$ SBUs can be regarded as six-connected nodes. BPPA ligands and $hfipbb^{2-}$ anions can be regarded as linkers, thus forming a 2D bilayer networks [Figure 4(*a*)]. The Schläfli symbol for this bilayer net is $\{4^{11}.6^4\}$. After searching in 11 databases containing 72505 topology types, we can confirm that the topology of complex **1** is completely new within the coordination polymer chemistry. The discovery of this new topology is useful at the basic level in the crystal engineering of coordination networks. The packing drawing of the simplified structure of **1** is shown in Figure 4(*b*), and the adjacent networks in **1** do not entangle with each other.

In addition, the UV-VIS absorption spectra of complexes **1** and **2** were measured in a crystalline state at room temperature (BPPA and $H_2hfipbb$ in a solid state) (Figure S1, see Online Supplementary Materials). BPPA and $H_2hfipbb$ show intense absorption peaks in the ranges of 200–300 nm and 200–420 nm, respectively, which can be ascribed to the π–π* transitions of ligands. Both of complexes **1** and **2** exhibit full-band absorption in the visible range. The energy bands of complex **1** at 460–600 nm and complex **2** at 550–700 nm are assigned to *d*–*d* transitions, while the energy band of complexes **1** and **2** at 200–420 nm can be attributed to the internal π–π* transitions of the ligands.

To estimate the stability of the coordination architectures, the thermal behaviours of complexes **1** and **2** were studied by thermogravimetric analysis (TGA) in an N_2 atmosphere (Figure S2, see Online Supplementary Materials). The results reveal that the thermal behaviours of complexes **1** and **2** are similar. For **1**, the first weight loss of 16.94% was observed before 300 °C along with the increase of temperature, corresponding to the departure of DMF molecules and the lattice and coordinated water (calc. 17.03%). The structure of **1** decomposed starting at 380 °C. The second weight loss of 71.95% was observed from 380 to 618 °C, corresponding to the loss of BPPA molecules and $hfipbb^{2-}$ anions (calc. 72.15%). The final residue of sample **1** (found 10.93%) is mainly composed of CoO (calc. 10.82%). For **2**, the first weight loss of 17.02% was detected before 340 °C along with the increase

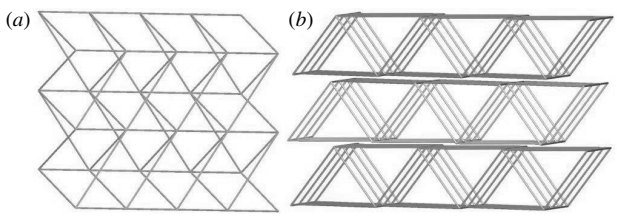

Figure 4 (*a*) Perspective view of the simplified 2D network of **1** (BPPA ligand and $hfipbb^{2-}$ anions were simplified into linkers); (*b*) packing drawing of simplified structure of **1**.

CCDC 993143 and 1007033 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

of temperature, corresponding to the departure of DMF molecules and the lattice and coordinated water (calc. 17.03%). The structure of **2** started to decompose at 400 °C. The second weight loss of 72.05% was detected from 400 to 665 °C, corresponding to the loss of BPPA molecules and $hfipbb^{2-}$ anions (calc. 72.18%). The final residue of sample **2** (found 10.76%) is mainly composed of NiO (calc. 10.79%).

To confirm that the crystal structures of **1** and **2** are truly representative of the bulk materials, powder X-ray diffraction experiments were carried out (see Figure S3, Online Supplementary Materials).

In conclusion, the new V-shape ligand BPPA was synthesized and used in the reaction with bivalent metal ions and $H_2hfipbb$ under solvothermal conditions to afford two new bilayer 2D coordination polymers $\{[Co_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ and $\{[Ni_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$, which are isostructural from the topological point of view and exhibit 2D bilayer networks of completely new topology type.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.023.

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