2,2'-Bipyidine-3,3',6,6'-tetracarboxylic Acid

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Different Dimensional and Structural Variations in Coordination Compounds of Cadmium, Manganese and Nickel Constructed from the Ligand 2,2'-Bipyidine-3,3',6,6'-tetracarboxylic Acid (H₄bptc)

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The reactions of hydrated $CdCl_2$, $MnCl_2$, and $NiCl_2$ with 2,2'-bipyidine-3,3',6,6'-tetracarboxylic acid (H_4bptc) afforded the mononuclear $[Cd^{II}(H_2bptc)(H_2O)_3]\cdot H_2O$ (**1**), linear $\{[Cd(H_2bptc)(H_2O)]\cdot 3H_2O\}_n$ (**2**), 3-D hetero-bimetallic $[NaCd(Hbptc)(H_2O)]$ (**3**), layer $[Mn(H_2bptc)(H_2O)]_n$ (**4**) and a dinuclear compound $[Ni_2(H_2bptc)$-$(H_2O)_2]\cdot 6H_2O$ (**5**). These compounds have been characterized by elemental analysis, IR, and their structures have been determined by X-ray crystallography. The thermal stabilities of **1-3** were measured by thermogravimetric analysis (TGA) and their solid state luminescence properties together with the free ligand H_4bptc were investigated at room temperature.

Key Words : Bipyridinetetracarboxylic acid, Cd(II) complex, Crystal structures, Luminescence

Introduction

The rational design and synthesis of inorganic-organic hybrid materials consisting of N-/O-donor ligands and transition metal ions are one of the most attracted areas in material science not only for their interesting properties such as host-guest chemistry, catalysis and magnetic behavior, but also for their structural diversity of the architectures.[1-3] To establish these classes of materials, many factors including solvent, temperature, different kinds of bases, pH value of solution, and the coordination preference of the metal ions should be considered.[4-8] However, the selected ligand is one of most important factors, since its functionality, flexibility, symmetry and the non-covalent forces such as hydrogen-bonding and π-π stacking could significantly influence the self-assembly of metal-organic frameworks (MOFs).[9] Multi-carboxylate ligands have been proved to be excellent candidates to construct this class of functional materials owing to their diversified coordination modes.[10,11] So far, the coordination chemistry of bipyridinedicarboxylate and phenanthrolinedicarboxylate ligands have been extensively investigated.[12-15] Compared with bipyridinedicarboxylate, the coordination chemistry of bipyridinetetracarboxylate ligands is much less common. Until now, a series of bipyridinetetracarboxylate ligands including 4,4'-bipyridine-2,2',6,6'-tetracarboxylic acid,[16] 2,2'-bipyridine-5,5',6,6'-tetracarboxylic acid,[17] and 2,2'-bipyridine-4,4',6,6'-tetracarboxylic acid have been synthesized.[18] Recently, Pruchnik has reported a new synthetic route to obtain 2,2'-bipyridine-3,3',6,6'-tetra-carboxylic acid ligand (H_4bptc) *via* the oxidation of 2,9-dimethyl-1,10-phenanthroline with $KMnO_4$ in water basic condition.[19] Subsequently, Twaróg reported a novel C-C

bond cleavage of H_4bptc that was catalyzed by the starting rhenium salt under the solvothermal reaction.[20] The reactions of H_4bptc with lanthanide(III) ions afforded four iso-structural complexes $[Ln_2(Hbptc)_2(H_2O)_4]_n\cdot 2nH_2O$ (Ln = Sm, Eu, Gd, and Tb).[21] However, the coordination chemistry of H_4bptc deserves more attention. It could be anticipated that H_4bptc could exhibit rich coordination modes, since there are four carboxylic acids and two pyridine rings that will provide numerous coordinating sites and flexible connection modes. Herein, we intend to further investigate the coordination chemistry mainly based on the following considerations: (i) the coordination sites of N and O donors in this ligand are less steric; (ii) weak supra-molecular interactions such as H-bonding and π-π stacking are readily formed; (iii) the deprotonated H_3bptc^-, H_2bptc^{2-}, and $Hbptc^{3-}$ species could be readily formed to balance the charge; (iv) two pyridyl rings can rotate around the C-C single bond, which could increase the potential possibility to form helical or chiral structure.

Also, there has been growing interest in the photochemistry of luminescent Cd^{II} coordination complexes.[22] Herein, the reactions of H_4bptc with hydrated Cd^{II}, Mn^{II} and Ni^{II} salts have been conducted at different reaction conditions. Five new coordination compounds have been obtained and their crystal structures were determined by X-ray crystallography. These Cd^{II} complexes were characterized by elemental analysis, IR, TGA, and their solid state photoluminescence properties were measured at room temperature.

Experimental Section

Materials and Physical Measurements. 2,2'-Bipyridine-

3,3',6,6'-tetracarboxylic acid (H₄bptc) was synthesized according to the reference's procedures.[19] Hydrated metal salts $CdCl_2$, $NiCl_2$ and $MnCl_2$, and the bases NH_4OH, and $NaOH$ were purchased from Aldrich and used as received. All solvents were purified prior to use following standard methods. IR spectra were obtained in the 4000-400 cm^{-1} range as KBr discs with a Nicolet 360 FTIR spectrophotometer. Elemental analysis was performed with an Elementar Vario EL Analyzer. Thermogravimetric analysis experiments were carried out with a Perkin–Elmer TGA7 thermogravimetric analyzer with the heating rate of 10 °C·min⁻¹ from 30 to 600 °C in a nitrogen atmosphere. Fluorescence spectra of compounds **1-3** and H₄bptc were recorded with an F-2500 FL Spectrophotometer analyzer at room temperature.

X-ray Crystallography. Intensity data were collected on an Oxford CCD diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) for compounds **1-5**. Details of the intensity data collection and crystal data are given in Table S1. Absorption corrections were done by the multi-scan method. Their structures were resolved by the heavy-atom Patterson method or direct method and refined by full-matrix least-squares using SHELX-97 and expanded using Fourier techniques.[23,24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms except partial H atoms on the aqua and lattice water molecules were generated by the program SHELXL-97. The positions of hydrogen atoms were calculated on the basis of riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R indices. All calculations were performed using the teXsan crystallographic software.[25] Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-924614 (**1**); CCDC-924615 (**2**); CCDC-924617 (**3**); CCDC-924618 (**4**); CCDC-924619 (**5**)). These data can be obtained free of charge *via* http:// www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ ccdc.cam.ac.uk.

[Cd^{II}(H₂bptc)(H₂O)₃]·H₂O (1): H₄bptc (33.0 mg, 0.1 mmol) and CdCl₂·2H₂O (21.9 mg, 0.1 mmol) were added into a mixed solvent of H₂O/EtOH (30 mL, v:v = 1:1) and the mixture was stirred at room temperature for 1 h. A colorless clear solution was obtained. The colorless block crystals suitable for X-ray crystallography were obtained after standing at room temperature for 2 weeks. Yield: 48% (24.7 mg). Selected IR (KBr, cm⁻¹): 3312, 2954, 2917 (s), 2849 (s), 1641 (s), 1546 (s), 1523 (s), 1463, 1444, 1398 (s), 1357, 1249, 1141, 1097, 983, 833, 719, 687. Anal. Calcd for C₁₄H₁₄CdN₂O₁₂: C, 32.67; H, 2.74; N, 5.44. Found: C, 32.58; H, 2.82; N, 5.40.

[Cd(H₂bptc)(H₂O)₂]·3H₂O (2): NH₄OH (0.1 mol/L, 2 mL) was added into a suspension of H₄bptc (33.0 mg, 0.1 mmol) in water (10 mL) and a colorless solution was obtained. CdCl₂·2H₂O (31.0 mg, 0.14 mmol) in EtOH was slowly added into the solution and the solution was stirred at room temperature for 1 h (if the white precipitates were generated, they should be removed by filtration immediate-

ly). Standing the solution at room temperature for 1 week, colorless block crystals suitable for X-ray crystallography were obtained with yield 56% (29.8 mg). Selected IR (KBr, cm⁻¹): 1733, 1716, 1697, 1652, 1635, 1615 (s), 1575. (s), 1557 (s), 1506, 1488, 1472, 1457, 1404 (s), 1363 (s), 1270, 1232, 1194, 1127, 1082, 853, 803, 766, 717. Anal. Calcd for C₁₄H₁₆CdN₂O₁₃: C, 31.57; H, 3.03; N, 5.26. Found: C, 31.60; H, 3.10; N, 5.33.

[NaCd(Hbptc)(H₂O)] (3): NaOH (8.0 mg, 0.2 mmol) was added into a suspension of H₄bptc (33.0 mg, 0.1 mmol) in water (10 mL) and a colorless solution was obtained. CdCl₂·2H₂O (31.0 mg, 0.14 mmol) in EtOH was slowly added into the solution and the solution was stirred at room temperature for 1 h. Standing the solution at room temperature for 1 week, colorless block crystals suitable for X-ray crystallography were obtained with yield 42% (20.3 mg). Selected IR (KBr, cm⁻¹): 1698, 1606 (s), 1557 (s), 1467, 1413 (s), 1377, 1299, 1268 (s), 1223 (s), 1191, 1080, 877, 858, 799 (s), 761 (s), 747, 693. Anal. Calcd for C₁₄H₇CdN₂NaO₉: C, 34.84; H, 1.46; N, 5.80. Found: C, 34.82; H, 1.50; N, 5.76.

[Mn(H₂bptc)(H₂O)]ₙ (4): A mixture of MnCl₂·4H₂O (27.7 mg, 0.14 mmol) and H₄bptc (33.0 mg, 0.1 mmol) in a mixed solvent EtOH/H₂O (15 mL, v:v = 2:1) was stirred for 5 min, sealed in a 23 cm³ Parr bomb, and heated to 140 °C for 3 days, and then cooled to room temperature at the rate of 0.1 °C min⁻¹. Colorless crystals of **4** were obtained with yield 52% (20.2 mg) based on H₄bptc. Selected IR (KBr, cm⁻¹): 1700 (s), 1636, 1594, 1558, 1463, 1407, 1374, 1302, 1268, 1231, 1194, 1125, 1082, 896, 880, 801, 792, 763, 747, 717. Anal. Calcd for C₁₄H₈MnN₂O₉: C, 41.71; H, 2.00; N, 6.95. Found: C, 41.69; H, 2.10; N, 6.87.

[Ni₂(H₂bptc)(H₂O)₂]·6H₂O (5): A mixture of NiCl₂·6H₂O (33.2 mg, 0.14 mmol) and H₄bptc (33.0 mg, 0.1 mmol) in a mixed solvent EtOH/H₂O (15 ml, v:v = 2:1) was stirred for 5 min, sealed in a 23 cm³ Parr bomb, and heated to 140 °C for 3 days, and then cooled to room temperature at the rate of 0.1 °C min⁻¹. Green block crystals of **5** were obtained with yield 60% (28.7 mg). Selected IR (KBr, cm⁻¹): 1721, 1630, 1588, 1572, 1479, 1452, 1374, 1251, 1182, 1088, 1073, 810, 796, 735, 708. Anal. Calc. for C₂₈H₃₂N₄Ni₂O₂₆: C, 35.11; H, 3.37; N, 5.85. Found: C, 35.20; H, 3.50; N, 5.79.

Results and Discussions

The reactions of H₄bptc with hydrated CdCl₂ in neutral environment or in the presence of NH₄OH or NaOH afforded the discrete [Cd^{II}(H₂bptc)(H₂O)₃]·H₂O (**1**), linear {[Cd(H₂bptc)(H₂O)₂]·3H₂O}ₙ (**2**), and 3-D heteronuclear [NaCd(Hbptc)(H₂O)]ₙ (**3**), respectively. The solvothermal reactions of H₄bptc with hydrated MnCl₂ and NiCl₂ afforded layer [Mn^{II}(H₂bptc)(H₂O)]ₙ (**4**) and dinuclear compound [Ni₂(H₂bptc)(H₂O)₂]·6H₂O (**5**), respectively. Compound **5** is isotypic to its Fe^{II} and Co^{II} analogues.[19] The ligand H₄bptc in these compounds exhibits different deprotonated forms of H₂bptc²⁻, Hbptc³⁻, and bptc⁴⁻ bearing formally -2, -3, and -4 charges, respectively. IR spectra of these compounds reveal

the presence of H-bonding interactions. The broad ν(O–H) stretching bands of the coordinated aqua ligands, lattice water molecules and carboxylic acid groups are observed in the range of 3400-3100 cm^{-1}. Due to the coexistence of carboxylic groups and bipyridine groups, the combined vibration modes of carboxylic groups and pyridine ring deformation appear and it is difficult to distinguish the contribution of carboxylic species from that of bipyridine groups. In general, the carboxylic groups are expected to give rather intense bands from asymmetric stretching vibration in the range of 1630-1500 cm^{-1} and symmetric stretching vibration in the range of 1460-1350 cm^{-1}.[26,27] As a result, the strong absorption bands at in the range of 1630-1546 cm^{-1} in compounds **1-5** can be assigned to the asymmetric stretching vibration ν_{as}(COO) of carboxylic groups.

The crystal structure of **1** is shown in Figure 1. The Cd^{II} atom is seven-coordinated in a pentagonal bipyramid by two carboxylate O atoms and two N atoms from a H$_2$bptc^{2-} ligand, and three water O atoms. Selected bond parameters are summarized in Table S2. The ligand is dianionic *due to* the deprotonation of 6,6'-carboxylic acid groups. The dihedral angle between the two pyridyl rings is 34.1(1)°. The angles between the pyridyl rings and carboxylate COO planes for 3,3'-carboxylic groups are 27.2(1) and 35.3(1)°, respectively while those for 6,6'-carboxylic groups are 9.4 and 11.4(1)°, respectively. These values are considerably different from those of free ligand H$_4$bptc,[19] possibly *due to* the coordination of 6,6'-carboxylate groups of H$_2$bptc^{2-} with metal atom and formation of strong intermolecular hydrogen bonds with coordinated water molecules (Figure S1). The O5 and O7 donors are located in the axial positions, while the N1, N2, O2, O3, and O6 donors are in the equatorial plane. The deviation of equatorial angles of N1-Cd-N2, N1-Cd-O5, N2-Cd-O2, O2-Cd-O6, and O3-Cd-O6 from the theoretical average angle of 72° can be explained by the narrow bite angle resulting from the coordination of rigid tetradentate ligands. The bond lengths of Cd-N1 and Cd-N2 are 2.363(4) and 2.408(4) Å, respectively. The equatorial Cd-O2 and Cd-O3 bond lengths are 2.431(3) and 2.349(3) Å, respectively which are slightly longer than that of Cd-O6 (2.295(4) Å). The axial Cd-O5 and Cd-O7 bond lengths are 2.347(4) and 2.296(4) Å, respectively. These bond para-
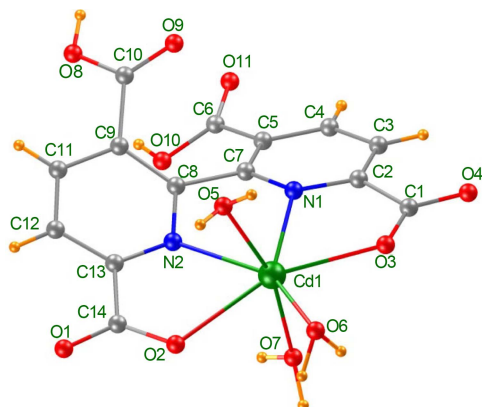
meters are comparable to the related cadmium-based complexes.[28,29] Extensive H-bonding interactions among carboxylate groups, aqua ligands and lattice water molecules are found (Table S3).

The structural fragment of **2** is shown in Figure 2. The asymmetric unit of **2** is composed of one Cd atom, one H$_2$bptc^{2-} ligand, two coordinated water molecules, and three lattice water molecules. The Cd^{II} atom is seven-coordinated in a pentagonal bipyramid by three carboxyl O atoms and two N atoms form two symmetry-related H$_2$bptc^{2-} ligands (O2, O3, O7^i, N1 and N2; symmetry code i: $x-1$, y, z) and two aqua O atoms (O5 and O6). Similar to **1**, the ligand is dianionic *due to* the deprotonation of 6,6'-carboxylic acid groups. The two pyridyl rings are twisted with respect to each other with a dihedral angle of 31.1(1)°. The dihedral angles of 3,3',6,6'-carboxylate groups with respect to the attached pyridyl groups are 29.8(1), 30.9(1), 9.8(1), and 11.9(1)°, respectively. The equatorial positions are occupied by N1, N2, O2, O3 and O7^i donors, while the axial positions are occupied by two aqua ligands (O5 and O6). The two Cd-N distances are 2.366(7) and 2.405(6) Å, respectively and the Cd-O distances are in the range of 2.298(5)-2.372(6) Å, which are similar to those related Cd^{II} complexes.[28,29] The equatorial angles also deviate from the theoretical average angle of 72°. The bridging behavior of carboxyl O7^i atom leads to a 1-D linear chain along *a* axis (Figure 3). In the extended structure, the nearest Cd···Cd separation is 9.215(6) Å.

There are three lattice water molecules in each asymmetric unit and they are clustered by the H-bonding interactions, which are indicated by the shorter O···O separation (O11···O12 = 3.276 Å).
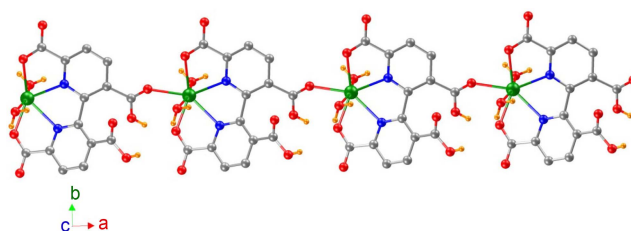

Figure 2. The structure fragment for **2** (symmetry code i: $x-1$, y, z).

Figure 1. Perspective view of **1**.
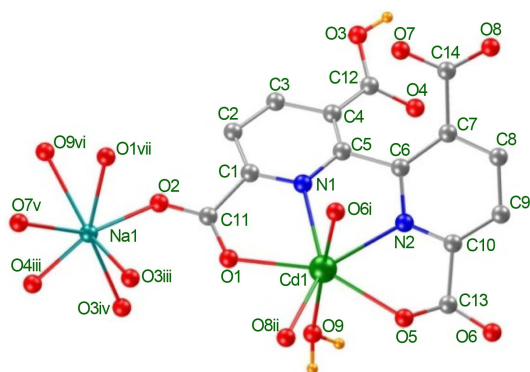

Figure 3. The 1-D linear chain in **2** along *a* axis.

Figure 4. The structural fragment of NaCd(Hbptc)(H$_2$O)] (**3**).

The structural fragment of **3** is shown in Figure 4. The asymmetric unit consists of one Hbptc^{3-} ligand, one Cd^{II} ion, one aqua ligand, and one Na$^+$ ion. Selected bond parameters are summarized in Table S5. The Cd1 is seven-coordinated in a pentagonal bipyramid by four carboxylate O atoms and two N atoms from three symmetry-related Hbptc^{3-} (O1, O5, O6^i, O8^{ii}, N1 and N2 symmetry code (*i*): *x*−1/2, −*y*+2; (*ii*): −*x*+1/2, *y*, *z*−1/2), and an aqua O atom (O9). The Na$^+$ is also seven-coordinated by seven O donors. The dihedral angle of two pyridyl rings is 31.2(1)º and the dihedral angles of 3,3',6,6'-four carboxylate groups with respect to the attached pyridyl rings are 33.1(1), 24.0(1), 11.8(1), and 32.8(1)º, respectively. The four carboxylate groups bond to the Cd ions in the different coordination modes. The 3-carboxylic acid (O4-C12-O3) bonds to a Na$^+$ ion *via* μ_1-η^1: η^0 monodentate mode, while 3'-carboxylate group (O7-C14-O8) bridges a Cd^{2+} and a Na$^+$ with μ_2-η^1: η^1 *syn-syn* bridging mode. The 6-carboxylate (O1-C11-O2) bridges a Cd^{2+} and a Na$^+$ with μ_2-η^2: η^0 bridging mode and 6'-carboxylate (O5-C13-O6) bridges two Cd^{2+} ions in μ_2-η^1: η^1 *syn*-anti bridging mode. Along *ac* plane, the bridging behaviors of two carboxylate groups initially lead to a 2-D layer structure (Figure 5). These adjacent layers stack in an ···*AAA*··· sequence along the *b* axis. If the metal centers are taken as nodes and the Hbptc^{3-} ligands are taken as linkers of a topological network, a 4^4 grid topological architecture is generated, as shown in Figure 6. The adjacent layers are
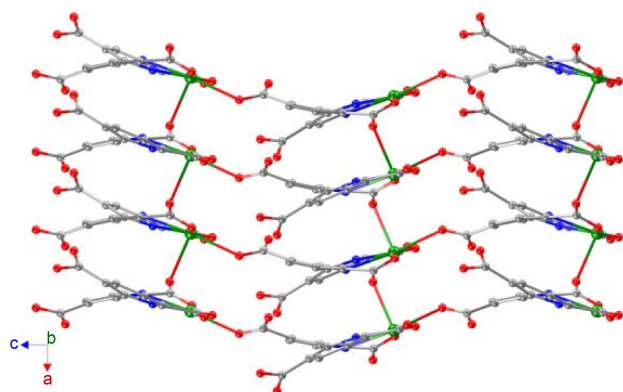

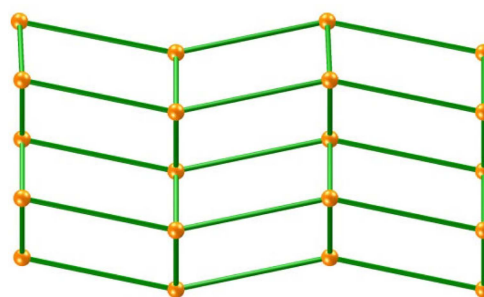**Figure 5.** The layer structure in **3** along *ac* plane.

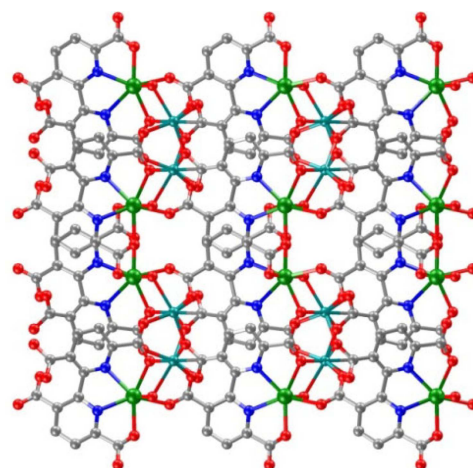**Figure 6.** Topological view of the layer structure of **3**.

Figure 7. Perspective view of **3** showing the adjacent layers are connected by the Na$^+$.

further linked by Na$^+$ ions *via* the coordination of seven O donors to give an extended 3-D network (Figure 7). There are extensive H-bonding interactions between coordinated aqua ligands with carboxylate groups (Table S6).

The two Cd-N bond lengths are 2.405(12) and 2.419(13) Å, respectively. The Cd-O bond distances are in the range of 2.300(11)-2.401(11) Å, which are comparable to those in complexes **1** and **2**, and are also similar to those in related Cd^{II} compounds.[28,29] The Na-O bond distances are in the range of 2.299(13)-2.576(15) Å, which are similar to related ionic Na-O bond distance in the range of 2.25-2.78 Å.[31] The π-π interactions of aromatic rings are found with the centroid-to-centroid distance of 3.686(6) Å.

The structural fragment of compound **4** is shown in Figure 8. Each Mn^{II} atom is seven-coordinated in a pentagonal bipyramid by four carboxyl O atoms, one aqua O atom and two N atoms. Two of these O donors (O6^i and O8^{ii}) originate from two symmetry-related structural units (Symmetry codes (*i*) x−1/2, −y+2, z; (*ii*) −x+1/2, y, z−1/2). The ligand is dianionic *due* to the deprotonation of 6,6'-carboxylic acid groups. The structure of **5** reveals that the dihedral angle between two pyridyl rings is 30.9(1)º. The dihedral angles of 3,3'-carboxylic groups with respect to the attached pyridyl rings are 31.9(1) and 21.9(1)º, respectively, while those for 6,6'-carboxylic groups are 10.8(1) and 33.4(1)º, respectively.
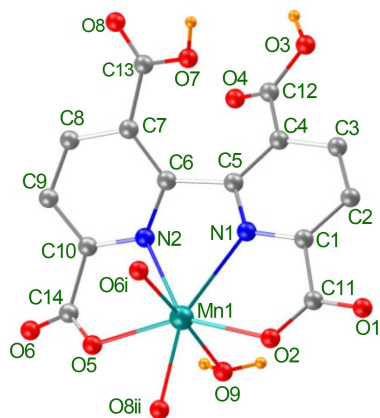
The O6 and O9 donors are located in the axial positions,

Figure 8. Structural fragment of **4** showing the coordination geometry of Mn ion (symmetry code *i*: x−1/2, −y+2, z; *ii*: −x+1/2, y, z−1/2).
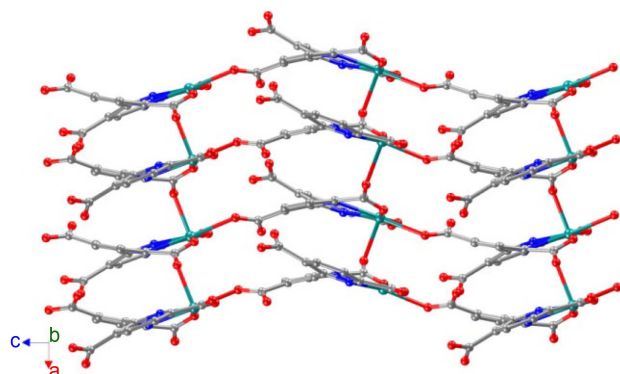

Figure 9. The packing diagram of **4** along *ac* plane.

and the N1, N2, O2, O5, and O8 donors are in the equatorial plane. The equatorial angles of N1-Mn-N2, N2-Mn-O5, N1-Mn-O2, O8-Mn1-O5, and O2-Mn1-O8 deviate from the theoretical average angle of 72º. The bond lengths of Mn-N1 and Mn-N2 are 2.366(7) and 2.375(8) Å, respectively. The Mn-O bond lengths are in the range of 2.175(6)-2.335(6) Å, which are similar to those in the related manganese-based complexes.[32]

The bridging behaviors of two carboxylic acid groups result in an approximately square-grid structure, which is further edge-shared with its equivalent to form an undulated 2-D layer sustained by coordination bonds parallel to the *ac* plane (Figure 9). If the metal centers are taken as nodes and H_2bptc^{2-} are taken as linkers of a topological network, a 4^4 grid topological architecture is generated, as shown in Figure 10. In each layer, there are extensive π-π interactions between pyridine rings with an average centroid-to-centroid distance of 3.678(7) Å. Moreover, the layer structures are further linked to each other to form a 3-D supra-molecular network, mainly by virtue of three pairs of O-H···O hydrogen bonds (Table S7).

The crystal structure of **5** is shown in Figure S3, which is isostructural to its Fe[II] and Co[II] analogues. In each asymmetric unit, there are two Ni[II] ions and two H_2bptc^{2-} ligands, four aqua ligands, and six lattice water molecules. These
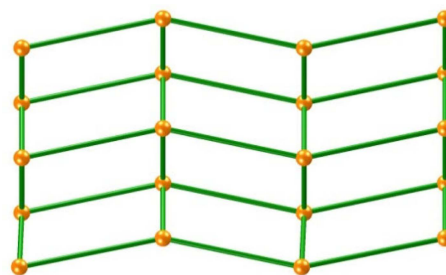

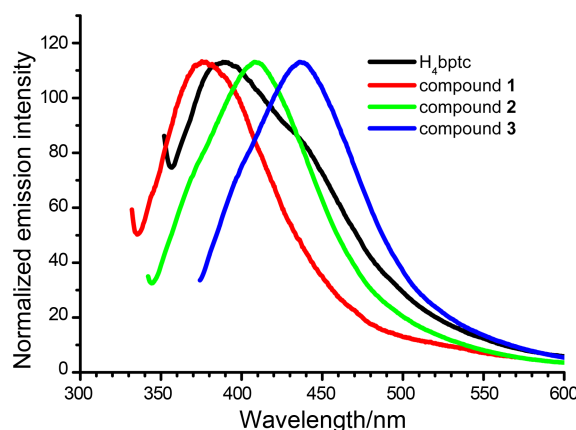**Figure 10.** Topological view of **4**.

Figure 11. Solid-state emission spectra of free ligand H_4bptc and compounds **1-3**.

water molecules and carboxylate groups are seriously disorder, which result in the larger R value. Thus, the bond parameters around the metal centers are not available. However, the structure clearly exhibits the octahedral coordination geometry around the metal center.

In the above structures, the ligand's conformations vary on the basis of its coordination with different metal ions. We considered that conformational changes occur in this ligand to allow the metal-ligand distance to optimize. The two pyridine rings are rotatable around central C-C bond; thus, a limited range of metal-donor atom distances can be optimally accommodated within this ligand. The coordination preference and ionic size may have profound effects on the ligand conformation, which may be mostly responsible for structural diversity of these compounds. Extensive weak interactions such as H-bonding and π-π stacking among the aromatic rings are found in these compounds, which are commonly encountered in the metal compounds bearing pyridine multi-carboxylate ligands. Usually, these interactions may be regarded as the stabilizing factor for the whole framework.[33]

Thermal Stability of the Compounds 1-3. The thermal behaviors of three cadmium complexes **1-3** were studied by thermogravimetric analysis (TGA) under a N_2 atmosphere with a heating rate of 10 °C/min (Figure S4). Compounds **1** and **2** lost their water molecules in the range of 25-145 °C, with the weight loss of 13.14% and 16.05%, respectively, corresponding to the loss of the lattice and coordinated water

molecules per formula unit (calc. 13.98% and 16.89%, respectively). The dehydration process is followed by a plateau of stability form 145-298 °C, and then the compounds decompose rapidly with a two-step weight loss. The TGA curve of **3** shows a weight loss from room temperature to 92 °C, corresponding to the loss of one coordinated water molecule (observed 3.90%, calculated 3.72%). The dehydrated solid shows no further weight loss until 259 °C and then further heating leads to the final decomposition of the compound **3**.

Fluorescence Properties. The luminescent properties of complexes with d^{10} metal centers are of great interest for their potential applications in photochemistry, chemical sensors, and electroluminescent display.[34] The luminescence properties of compounds **1-3**, as well as the free H$_4$bptc ligand, were investigated in the solid state at room temperature. As shown in Figure 11, intense emission bands were observed at λ_{em} = 388 nm upon the excitation at λ_{ex} = 342 nm for H$_4$bptc, while compounds **1**, **2**, and **3** show the emission maximums at λ_{em} = 376, 408, and 437 nm upon the excitation at λ_{ex} = 322, 364, 332 nm, respectively.

The observed emission bands of **1-3** may result from intraligand $\pi \rightarrow \pi^*$ transition between the π-bonding orbital (HOMO) and π^*-antibonding orbital (LUMO) of H$_4$bptc ligand due to their resemblance to the emission of H$_4$bptc ligand, rather than metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) in nature. Compared with H$_4$bptc, the blue/red-shifts of these compounds may be assigned to the ligand chelating or bridging effect due to the coordination of Cd^{II} center, changing the rigidity and conjugation of H$_4$bptc.[34] The emission of Cd^{II}-containing polymers may be complicated in mechanism since there are so many contributive interactions in this system. In these complexes, the two pyridyl rings form different dihedral angles. The smaller dihedral angle favors an orbital conjugation between two cycles. Moreover, the cooperative effect of the weak interactions such as H-bonding interaction and π-π stacking could also influence the observed emission spectra, since these classes of weak interactions may play an essential role to decrease the HOMO-LUMO energy gap of ligand.[35] The strong fluorescence emissions of these compounds make them potentially useful candidates for hybrid photoactive materials.

Conclusion

Three cadmium(II) compounds, a manganese(II), and a nickel(II) compounds have been obtained from the reactions of H$_4$bptc with hydrated salts in mild conditions. The different deprotonated forms of Hbptc^{3-}, H$_2$bptc^{2-}, and bptc^{4-} are found in these compounds. The two pyridyl rings could rotate around the central C-C bond to form the different dihedral angles. The luminescence properties of Cd(II) compounds bearing H$_4$bptc could be readily tuned by the subtle alteration of coordination environments of metal center. The stronger fluorescence emissions also indicate that these compounds are potential candidates for hybrid photoactive materials.

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