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((1H-tetrazol-5-yl) methyl) pyridine-based Metal Coordination Complexes: In situ Tetrazole Synthesis, Crystal Structures, Luminescent Properties

Ruoting Dong, Xinli Chen, Qianhong Li, Mingyuan Hu, Lanfen Huang, Chuwen Li, Moyuan Shen, Hong Deng*

School of Chemistry & Environment, South China Normal University, Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, and Key Laboratory of the Energy Conversion and Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, Guangzhou 510006, PR China

**To whom Correspondence should be addressed. E-mail: dh@scnu.edu.cn.*

Abstract

Six novel transition metal coordination complexes [Cu(3TMP)] (**1**), [Zn(3TMP)Cl] (**2**), [Cd_3(3TMP)$_4$(N_3)$_2$]·0.38H_2O (**3**), [Zn_3(4TMP)$_2$(OH)$_2$(H_2O)]·2(NO_3) (**4**) and [M_2(4TMP)(OH)(H_2O)(SO_4)] (M = Zn (**5**), M = Cd (**6**)) (3HTMP = 3-((1H-tetrazol-5-yl) methyl) pyridine; 4HTMP = 4-((1H-tetrazol-5-yl) methyl) pyridine), have been hydrothermally synthesized through *in situ* tetrazole synthesis. These complexes have been structurally characterized by single crystal and powder X-ray diffraction elemental analyses, Fourier transform infrared spectroscopy as well as thermal studies. The complexes **1-6** are two or three-dimensional (3D) frameworks with structural diversity owing to the versatile coordination modes of the *in situ* generated flexible ligands. Complex **1** presents a reticular structure consisting of two-dimensional (2D) layers formed by the linkage between the pyridine rings and [Cu-tetrazole-Cu] wave-like chains. Complex **2** features a 3D framework built up by two kinds of helical chains composed of Zn(II) and flexible ligand 3TMP. Complex **3** exhibits a 3D framework built up from 3TMP ligands and trinuclear [Cd_3(N_3)$_2$] building units. Complex **4** crystallizes as a 3D coordination complex constructed from two-dimensional layers and the linkers of 4TMP ligands, with NO_3^- anions situated in the channels. Complexes **5** and **6** exhibit a 3D framework constructed from $\{M_2(4TMP)(OH)\}_n^{n-}$ (M = Zn (**5**), M = Cd (**6**)) layers and sulfate anions. In addition, the counterions, such as Cl terminal ligand in **2**, N_3 terminal ligand in **3**, μ_2-OH bridging ligand in company with free NO_3^- anions in **4**, and μ_3-OH bridging ligand in company with free SO_4^{2-} anions in **5** and **6**, have decisive influence on the dimensionality and functionality of the final complexes. Furthermore, solid state luminescent properties of these complexes have been investigated.

Introduction

The design and synthesis of metal–organic frameworks (MOFs) are extensively studied because of their intriguing architectures and topologies,[1] and potential applications in molecular absorption, separation[2] and catalysis,[3] optics,[4] and magnetic materials.[5] Especially, luminescent coordination complexes have attracted intensive research interest for their potential applications as chemical sensors,[6] light-emitting devices,[7] biomedicine,[8] etc.[9]

From the viewpoint of crystal engineering, the intrinsic geometric preferences of metal centers and the various coordination modes of bridging organic linkers are crucial factors in governing architectures.[10] Thus, rational selection of metal centers and organic ligands with suitable configuration, functionality, flexibility, and symmetry plays a key role in the synthesis of coordination complexes featuring desired structures and properties. Among ligands, 5-substituted-1H-tetrazole derivative, a family of multidentate ligands, are considered to be one of the most suitable candidates for the construction of coordination networks through versatile coordination modes because they can bridge metal ions using up to four electron-donating nitrogen atoms of tetrazole groups, as well as donor atoms of 5-substituent functional groups.[11] Many efforts have been made to the construction of 5-substituted-1H-tetrazolate-based coordination complexes. For example, 5-R-tetrazoles (R=alkyl-,[12] pyrazinyl-,[13] pyrimidyl-,[14] pyridyl-,[15] phenyl-,[16] amino-,[17] etc.) generated by *in situ* reactions have been employed as excellent chelating and/or bridging ligands to construct novel metal coordination complexes, which were found to possess intriguing architectures as well as potential applications as functional materials. Recently, pyridyltetrazoles have become attractive ligands for the design of MOFs, owning to their abilities of bridging multiple metal sites and considerable variations in tether lengths.[18] However, the investigation of bifunctional pyridyltetrazole ligand as building blocks for constructing coordination frameworks has less developed so far. It is also noted in the studies of metal-tetrazolates, that coordinating anions, such as halides, sulfate, hydroxyl and azide can dramatically influence the structures and properties of the complexes. These observations encouraged us to explore the chemistry of metal-pyridyltetrazole with various anionic components.

In our work we choose 3-pyridylacetonitrile (3L) and 4-pyridylacetonitrile (4L) as precursors reacting with sodium azide under the help of transition metal salts (M = Cu, Zn and Cd) to construct interesting tetrazole-based coordination complexes, based on the following reasons: (1) the addition of -CH_2- spacer between the rigid tetrazole group and pyridine group offers flexible orientations, thus the conformational freedom may be better to satisfy the geometric needs for different metal ions to construct diversified and intriguing architectures;[19] (2) it exhibits excellent coordination capacities with five coordination sites of the tetrazolate ring and one N donor of pyridyl group; (3) to our knowledge, no coordination complexes based on 3TMP and 4TMP ligands have been observed so far, although a few coordination complexes coordinated with rigid aromatic-tetrazolate ligands were reported.[20]

Herein, coordination complexes are obtained in the presence of the different substituted site of pyridine group and metal sources, and the influence of the inorganic anions on their structures are investigated. In this contribution, we report the syntheses and crystal structures of a series of transition metal based coordination complexes, [Cu(3TMP)] (**1**), [Zn(3TMP)Cl] (**2**), $[Cd_3(3TMP)_4(N_3)_2]\cdot 0.38H_2O$ (**3**), $[Zn_3(4TMP)_2(OH)_2(H_2O)]\cdot 2(NO_3)$ (**4**), and $[M_2(4TMP)(OH)(H_2O)(SO_4)]$ (M = Zn (**5**), M = Cd (**6**)), which have been isolated by hydrothermal reactions of the corresponding transition metal salts with 3-pyridylacetonitrile for **1-3**, and 4-pyridylacetonitrile for **4-6**, respectively. These coordination complexes exhibit two or three-dimensional frameworks and contain various inorganic counteranions, Cl^- for **2**, N_3^- for **3**, OH^- in company with NO_3^- for **4**, and OH^- in company with SO_4^{2-} for **5** and **6**. In other words, these anions may be responsible for the structural diversity in **2-6**. In addition, these two ligands exhibit their excellent coordination ability of five nitrogen atoms to act as either a multidentate or a bridging building block, and several novel coordination modes were shown in this text (seen Chart 1). Furthermore, the X-ray powder diffraction (PXRD), thermal and fluorescent properties of these complexes have also been investigated.

Experimental Section

General remarks. All materials and reagents were obtained commercially and were used without further purification. Elemental (C H N) analyses were performed on a Perkin-Elmer 2400 element analyzer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000-400 cm^{-1} range using a Nicolet Avatar 360 Fourier transform infrared (FT-IR) spectrophotometer. Thermogravimetric analysis (TGA) experiments were performed on a NETZSCH TG 209 instrument with a heating rate of 5°C min^{-1}. Fluorescence spectra were recorded with an F-2500 FL spectrophotometer analyzer.

Synthesis of [Cu(3TMP)] (1)

A mixture of CuCl (0.067 g; 0.5 mmol) , NaN_3 (0.033 g; 0.5 mmol) and 3-Pyridylacetonitrile (2 mL) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 150-180 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals were obtained in a yield of 20 % based on Cu. Elemental Anal. Calcd (%) for **1** , $CuC_7N_5H_6$ (447.4): C, 37.55 H 2.68, N 31.29; found: C 37.00, H 2.50, N 31.00; IR (KBr, cm^{-1}): 3165s, 1692s, 1512m, 1427m, 1360s, 1126m, 1043w, 847w, 707m.

Synthesis of [Zn(3TMP)Cl] (2)

A mixture of $ZnCl_2$ (0.050 g; 0.5 mmol), NaN_3 (0.033 g; 0.5 mmol) and 3-Pyridylacetonitrile (2 mL) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 150-180 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals were obtained in a yield of 63 % based on Zn. Elemental Anal.

Calcd (%) for **2** , $ZnC_7N_5H_6Cl$ (521.9): C 32.19, H 2.30, N 26.82; found: C 32.00, H 2.30, N 27.00 ; IR (KBr, cm^{-1}): 3049w, 1615m, 1480s, 1438s, 1416s, 1265w, 1193m, 1077s, 772s, 693s.

Synthesis of [Cd_3 (3TMP) $_4$ (N_3) $_2$] · 0.38H_2O (3)

A mixture of $CdSO_4$ (0.104 g; 0.5 mmol), NaN_3 (0.033 g; 0.5 mmol) and 3-Pyridylacetonitrile (2 mL) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 150-180 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}. Colorless block crystals were obtained in a yield of 70 % based on Cd. Elemental Anal. Calcd (%) for **3** , $Cd_3C_{28}N_{26}H_{24.76}O_{0.38}$ (1068.77): C 27.12, H 2.26, N 34.28; found: C 27.00, H 2.20, N 34.00; IR (KBr,cm^{-1}): 3473s, 2066s, 1636m, 1471m, 1435m, 1390s, 1313m, 1288m, 1201w, 1045w, 775m, 709m.

Synthesis of [Zn_3 (4TMP) $_2$ (OH) $_2$ (H_2O)]·2(NO_3) (4)

A mixture of $Zn(NO_3)_2$ (0.190 g; 1 mmol), NaN_3 (0.170 g; 0.24 mmol) and 4-Pyridylacetonitrile (0.100 g; 0.065 mmol) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 170 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and yellow block crystals were obtained in a yield of 77 % based on Zn. Elemental Anal. Calcd (%) for **4,** $Zn_3C_{14}N_{12}H_{16}O_9$: C 24.28, H 2.32, N 24.27; found: C 24.30, H 2.30, N 27.03 ; IR (KBr, cm^{-1}):3412vs, 3100w, 2353w, 1678w, 1625m, 1508m, 1448m, 1336vs, 1186w, 1139m,1114s, 1064m, 1035m, 825w, 700s.

Synthesis of [Zn_2 (4TMP)(OH)(H_2O)(SO_4)] (5)

A mixture of $ZnSO_4$ (0.162 g; 1 mmol), NaN_3 (0.170 g; 0.24 mmol) and 4-Pyridylacetonitrile (0.100 g; 0.065 mmol) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 170 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and yellow block crystals were obtained in a yield of 33 % based on Zn. Elemental Anal. Calcd (%) for **5,** $Zn_2C_7N_5H_9O_6S$: calcd.: C 19.92, H 2.15, N 16.59; found: C 19.95, H 2.12, N 16.59; IR (KBr, cm^{-1}):3441vs, 2949w, 2376w, 1626m, 1564m, 1441m, 1348vs, 1280w, 1171m, 1101s, 1066m, 991m, 877w, 792w, 717m, 607m.

Synthesis of [Cd_2 (4TMP)(OH)(H_2O)(SO_4)] (6)

A mixture of $CdSO_4$ (0.208 g; 1 mmol), NaN_3 (0.170 g; 0.24 mmol) and 4-Pyridylacetonitrile (0.100 g; 0.065 mmol) in H_2O (10 mL) was sealed in a 23 ml Teflon reactor and kept under autogenous pressure at 170 °C for 3 days. The mixture was cooled to room temperature at a rate of 5 °C h^{-1}, and yellow block crystals were obtained in a yield of 45 % based on Cd for **6**. Elemental Anal. Calcd (%) for **6,** $Cd_2C_7N_5H_9O_6S$: C 16.29, H 1.76, N 13.57; found: C 16.30, H 1.78, N 13.55; IR (KBr, cm^{-1}):3433vs, 2960w, 2363w, 1620m, 1485m, 1433vs, 1258w, 1161m, 1105s, 1062m, 985m, 821w, 796w, 711m, 627m.

Crystal Structure Determination

Suitable single crystals of complexes **1-6** were selected and mounted in air onto thin glass fibers. Accurate unit cell parameters were determined by least-squares fit of 2θ values, and intensity data were measured on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Ka radiation (λ = 0.71073 Å). Data collection and reduction were performed using the APEX II software.[21] Multi-scan absorption corrections were applied for all the data sets using the APEX II program.[21] All six structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model. Only complex **3** has partial free water molecule (38%) existing in the center of one-dimensional channel in the asymmetric unit. Maybe structure **3** had missed partially occupied water molecules. And the residual Q peak is little huge (more than 2 electrons). Complex **4** exhibits 1:1 disorder of the free NO_3^- anions existing in the channels of complex **4**. These disorder free NO_3^- anions were restrained to be flat with a standard deviation of 0.1 Å, and the hydrogen atoms of coordinated and noncoordinated molecules were restrained to have O-H bond distances of 0.82 Å. The crystallographic data for all structures are listed in Table 1. The selected bond lengths and bond angles of the six complexes are listed in Table 2, and the hydrogen bond of complexes are listed in Table 3. CCDC No: 715716-17, 736758 and 787030-787032 for all structures are contained in the supplementary crystallographic data for this paper.

Results and Discussion

It has been realized that hydrothermal method is a powerful technical process in the fabrication of tetrazolate-based single crystalline materials.[22] All complexes in this communication were synthesized in good yields through employing this technology with *in situ* generated ligands of 3TMP and 4TMP. Single-crystal X-ray diffraction analysis demonstrates that the tetrazole groups in all six complexes were deprotonated to form tetrazole anions. The emergence of the peaks in the 1380-1650 cm^{-1} region clearly confirmed the formation of the tetrazole groups, as can be seen in Experimental Section or Figure S3 in Supporting Information.

In this study, it is noticeable that there are several factors to govern the formation of final products: i) the flexibility of ligands; ii) the catalysis of metal ions; iii) the reaction temperature; iv) the counterions. In our experiments, we employed two similar ligands in which the -CH_2CN connects to different positions of pyridine ring, to furnish a variety of structures. It should be noted that complex **1-3** were obtained at 150-180°C while the complex **4-6** were obained at 170 °C, as can be seen in Scheme **1**.

Crystal structure of 1.

Single-crystal X-ray diffraction study reveals that complex **1** is a two-dimension (2D) network constructed from infinite [Cu-tetrazole-Cu] chains and pyridine rings, crystallizing in the monoclinic chiral space group $P2_1$ with the Flack parameter being 0.11(3). As shown in Figure 1a, the asymmetric unit of **1** contains one Cu ion, one 3TMP ligand. Each Cu center is four–coordinated by four N donors, of which one from pyridine ring and the other three from three separated tetrazole groups. It displays a distorted tetrahedral coordination geometry with Cu-N bond distances in the range of 1.994(7)-2.039(3) Å, which are in good agreement with the values of those reported Cu-tetrazole complexes.[23] The 3TMP ligand acts as a μ_4-bridged ligand (Chart 1a III) through 1, 2, 3 nitrogen atoms of the tetrazole ring and one nitrogen atom from the pyridyl ring respectively connected to four copper ions in the structure.

The structure of the network can be best understood as a layer formed by the linkage of the pyridine rings and [Cu-tetrazole-Cu] wave-like chains. Furthermore, along two adjacent [Cu-tetrazole-Cu] chains, two Cu centers link four N atoms from two coordinated tetrazole groups to furnish a six-numbered ring as a building block (Figure 1b). These building blocks on the *ab*-plane are connected to each other to form a one-dimensional chain along the *b*-axis direction and the pyridine rings link up the one-dimensional chains in a way of interval inversion so as to constitute a two-dimensional network structure. To better understand the nature of the framework, a topological approach to the simplification of two-dimensional structures can be accomplished by reducing them to simple nodes and links. Therefore, if the tetrahedral Cu ions are regarded as four connected nodes and the 3TMP ligands are simplified to links of a topological network, the 2D network can then be seen in a simplified way as a **sql** net with point symbol “($4^4.6^2$)”(Figure 1c).

Crystal structure of 2.

Complex **2** crystallizes in the monoclinic space group *Cc* and features a three–dimensional (3D) framework built up by two kinds of helical chains composed of Zn(II) and flexible ligand 3TMP. As is shown in Figure 2a, the asymmetric unit of **2** contains one 3TMP ligand, one chlorine ligand and one Zn(II) ion. Each Zn(II) ion adopts a distorted tetrahedral coordinated environment that are formed by one chlorine ligand and three nitrogen atoms from three separated ligands 3TMP. The Zn-N bond lengths fall between 2.0140(18) and 2.0163(18) Å, and Zn-Cl bond length is 2.1928(8) Å. The chlorine ligand acts as a terminal ligand to each Zn(II) ion. Each 3TMP ligand adopts a μ_3–bridged coordination mode (Chart 1a I) with a nitrogen atom from pyridine groups connected to one Zn(II) ion, while N1 and N4 atoms of tetrazole groups coordinated to other two Zn(II) ions. The pyridine ring and the tetrazole ring are linked by $–CH_2–$ with the C1–C2–C3 bond angle being 112.79° which is slightly larger than that of complex **1** (figure 2a). The 3D coordination framework of complex **2** is generated by two kinds of helical chains that are formed by flexible 3TMP ligands and Zn(II) ions in the form of screwed connection of each other (figure 2b). That is, Zn(II) ions are in turn linked by N atoms from the pyridine groups and the tetrazole groups of 3TMP ligands and the description of the chains can be short for […Zn(II)-3TMP- Zn(II)- 3TMP-Zn(II)-TZ- Zn(II)…]. It is called R helical chain when […Zn(II)-3TMP- Zn(II)- 3TMP-Zn(II)-TZ- Zn(II)…] is linked by clockwise rotation from *a*-axis, while L helical chains are connected by anti-clockwise rotation (figure $S1_2$ in supporting information, figure 2c). Thus, the two kinds of helical chains are linked to each other by sharing the Zn(II) ions, giving rise to a 3D coordination framework (Figure. 2b). The coordination framework of **2** is achiral because of the existence of R and L helical chains which are in opposite directions. In addition, the intramolecular C-H···Cl hydrogen bonds between the terminal chlorine ligands and C-H from pyridine groups contribute to the stability of coordination framework of complex **2.** The 3D network can be described as the **ths** topological net with point symbol “(10^3)”, if the tetrahedral Zn(II) ions and the 3TMP ligands are both regarded as 3-connected nodes (Figure 2d).

Crystal structure of 3.

Single crystal X-ray diffraction analysis reveals that complex **3** crystallizes in the triclinic space group *P-1* and exhibits a 3D framework built up by 3TMP ligands and trinuclear $[Cd_3(N_3)_2]$ building units (Figure $S1_2$ in supporting information). As depicted in Figure 3a, there are two 3TMP ligands, two Cd(II) ions, one μ_2-N_3^- ligand and partial free water molecule (38%) (structure **3** had missed partially occupied water molecules (seen Crystal Structure Determination section for details)) in the asymmetric unit of **3**. Two crystallographically independent Cd(II) centers are six-coordinated, both displaying a distorted octahedral coordination geometry with Cd-N bond distances in the range of

2.284(5)-2.498(4) Å. Cd1 center is surrounded by six N atoms: four out of six come from three tetrazole groups, and the other come from two N_3^- ligands. Cd2 center is coordinated by two N atoms from pyridine groups, three N atoms from three tetrazole groups and one N atom from N_3^- ligand. Two μ_2-N_3^- ligands act in the 1,1-bridging mode (Chart 1c III) and are connected to three Cd(II) centers, furnishing a trinuclear $Cd_3(N_3)_2$ building unit (Figure 3c).

The 3TMP ligands in **3** adopt two coordination modes as μ_3-3TMP and μ_4-TMP which play an important role in constructing the coordination framework (Chart 1a II and III). The μ_4-TMP ligands use their tetrazole groups (μ_3-TZs) to link the structural unit $[Cd_3(N_3)_2]$ to form 1D chains along the *a*-axis by connecting Cd2, Cd1 and Cd2 centers, while their pyridine groups use N atoms to connect Cd centers of the adjacent 1D chains inversely to construct 2D network. The μ_3-3TMP ligands link the 2D networks to construct a 3D coordination complex *via* μ_1-pyridine groups and μ_2-TZs connecting inversely different Cd centers of adjacent 2D networks (Figure 3b). The 3D coordination framework of complex 3 can be simplified as a usual 6^6 topological structure with $[Cd_3(N_3)_2]$ building unit are substituted as a node (Figure 3d). Free water molecules exist in the center surrounded by 3TMP ligands and Cd ions of one-dimensional channels are viewed from the *b*-axis.

Crystal structure of complex 4.

The complex crystallizes in orthorhombic space group *Pbcn* as a 3D coordination complex constructed from two-dimensional layers and the linkers of 4TMP ligands, with NO^{3-} anions situated in the channels. The disorder observed in complex **4** can be attributed to a crystallographic mirror plane, across which lies part of the framework (seen Crystal Structure Determination section for details). As shown in the Figure 4a, the coordination environments of two crystallographically independent Zn centers in complex **4** are slightly different, in which Zn1 center is coordinated with three nitrogen atoms from three individual μ_4-4TMP ligands and one μ_2-OH anion, forming a slightly distorted tetrahedral geometry While Zn2 center adopts a rare five coordinated model in which Zn2 center is surrounded by two nitrogen atoms from two individual μ_4-4TMP, two μ_2-OH anions and one oxygen atom from a water molecule. 4TMP acts as a quadridentate ligand containing μ_3-tetrazole group and μ_1-pyridine group (Chart 1b IX). The Zn-N distances in complex **4** are 2.001(3)-2.215(3) Å, comparable to the values of those reported in other Zn-tetrazole complexes.[24] The Zn-O bond, O-N bond distances of nitrate anions are 1.893(3)-1.970(3) Å and 1.197(6)-1.229(7) Å , respectively. In the structure of **4**, each tetrazole group of 4TMP combines two Zn1 centers while each Zn1 center is also linked to two tetrazole groups shoulder by shoulder […tetrazole-Zn1-tetrazole-Zn1…], leading to the formation of the 1D zigzag chains along the *a*-axis(Figure 4c). It can be seen that both μ_2-O2w atoms and Zn2 centers act as roles of linkers of two adjacent chains. The independent Zn2 centers connect two N atoms from tetrazole groups of different chains, while μ_2-O2w atoms bridge Zn1 and Zn2 centers with the Zn1-O2w-Zn2 bond angle being 121.09(9)$^{\circ}$ to give rise to 2D layers through the *ac*-plane (Figure 4c). The pyridine groups of 4TMP ligands play the role of linkers to assemble the 2D layers to further form a 3D coordination framework *via* their N atoms connecting the Zn1 centers of two layers (Figure 4b). The channels viewed from *c*-axis of the novel 3D micropore coordination framework are filled with free NO_3^- anions, which are about 10.008 × 21.972 Å. The hydrogen bonds in complex **4** play a role of strengthening the stability of the 3D framework, especially the O(1W)-H(1W)…O(4B) (2.58 (Å)), O(1W)-H(1W)…O(5B) (1.93

(Å)), O(2W)-H(2W)…O(3) (2.08(3) (Å)) and O(2W)-H(2W)…O(4B) (2.44(3) (Å)) (Figure $S1_4$ b in supporting information). As shown in Figure. 4e, one Zn1 and two Zn2 are strengthened by two μ_2-O2 atoms to generate a trinuclear [Zn_3O_2] unit. If considering the trinuclear unit as a 6-connected node, the 4TMP ligand as a 3-connected node, the 3D structure of complex **4** can be simplified to a binodal (3,6)-connected network with point symbol "$\{4.6^2\}2\{4^2.6^9.8^4\}$" (Figure. 4d).

Crystal Structure of Complex 5 and 6.

Crystal structure analyses show that complex **5** crystallize in orthorhombic space groups *Pnma,* while complex **6** in *Pna21*. It is interesting that there is no distinction between the chemical components of complexes **5** and **6** except for some subtle differences in the crystallographic symmetry. Similar examples have been reported by Yue *et al.*[26] In complex **5**, S1, Zn1, O5 and pyridyl groups of the 4TMP ligands sit on a mirror plane parallel with the *a-c* plane, whilst Zn2 ion is located at a crystallographic inversion center. However, similar mirror planes and inversion centers are not observed in Complex **6.** Herein, only complex **5** is described here in detail. The structure of complex **5** is a 3D framework constructed from $\{Zn_2(4TMP)(OH)\}_n^{n-}$ layers and sulfate anions. As illustrated in Figure 5a, the asymmetric unit of **5** contains two crystallographically independent Zn(II) ions, one 4TMP, one μ_3-OH anion and one sulfate anion. Both Zn1 and Zn2 centers have distorted octahedral coordination geometry: Zn1 ion is coordinated by three nitrogen atoms from three different 4TMP ligands, one μ_3-OH anion, one oxygen atom from sulfate anion, and one oxygen atom from water molecule; Zn2 ion is coordinated by two nitrogen donors of two independent 4TMP, two μ_3-OH anions, and two oxygen donors of two sulfate anions. The Zn-N and Zn-O bond lengths range from 2.061(4) to 2.274(6) Å, which are shorter than those of complex **6** (2.235(3)-2.449(4) Å) due to the smaller ion radius of Zn(II). In this complex, the hydroxyl acts as a μ_3-bridging mode linking one Zn1 atom and two Zn2 atoms, generating a scalene triangle with Zn···Zn distances 3.366, 3.618, 3.618 Å (Cd···Cd distances 3.534, 3.821, 3.882 Å for complex **6**). The Zn-O5-Zn angles are about 109.48, 118.88 and 118.88°, so the μ_3-OH group is displaced out of Zn_3 plane, which results in the formation of a noncoplanar [Zn_3(μ_3-OH)] triangular unit. Each Zn2 ion of the triangular unit [Zn_3(μ_3-OH)] links two μ_4-tetrazole groups, whilst each μ_4-tetrazole group links two Zn2 ions to form a strip-shaped △-chain along the *c*-axis direction. The chains are connected into a network through bridging pyridyl groups of the 4TMP ligands. The pyridyl groups connect the μ_4-tetrazole group of a chain and bridge to one Zn1 ion of an adjacent chain to produce the layer substructure of Figure 5b. The layers stack along the *c*-axis direction. The μ_3-SO_4 anion acts as a bridging-ligand. On one end, two O atoms of the sulfate anion connect two Zn2 ions of the trimetric unit [Zn_3(μ_3-OH)]. Simultaneously, on the other end, one O atom of the sulfate anion links to the Zn1 of another strip-shaped △-chain of an adjacent layer to construct the 3D network (Figure 5d). In other words, each strip-shaped △-chain is connected with six identical chains *via* the μ_3-SO_4^{2-} and μ_5-4TMP ligands to generate a 3D metal-organic framework, of which four chains are connected by μ_3-SO_4^{2-} and the other two chains are connected by μ_5-4TMP ligands (Figure 5d). From the topological point of view, the octahedral Zn1 and Zn2 ions can be defined as 5- and 6-connected nodes respectively, both the O1 atoms and sulfate anions can be regarded as 3-connected nodes, the organic ligands can be considered as 5-connected nodes. Thus, the overall structure of **5** and **6** can be simplified as a 3D (3, 3, 5, 5, 6)-connected framework with $\{4.8^2\}\{4^3\}\{4^4.6^2.8^4\}\{4^5.6^5\}\{4^8.6^6.8\}$ topology (Figure 5c). Previous examples of (3, 3, 5, 5, 6)-connected frameworks are very rare. With the help of the software package TOPOS4.0[27] the same topology is found for complex $[Zn_2(trz)(OH)(SO_4)]$[28] (CSD refcode LIHRIE). The sulfate phase $[Zn_2(trz)(OH)(SO_4)]$ also manifests a complex three-dimensional structure, which can be described as $\{Zn_2(SO_4)(OH)\}_n^{n-}$ layers constructed from strip-shaped chains and trinuclear $[Zn_3(\mu_3\text{-}OH)_3]$ clusters in the *ab* plane, linked in the third dimension through triazolate ligands[28]. Compared with structure **5**, it's the sulfate moiety, instead of μ_5-4TMP ligand, that bridges adjacent chains to produce the layer substructure, adopting a η^3, μ_5 coordination mode. Moreover, what links the layers into 3D framework is the N1,N2,N4-bridging triazolate ligand, instead of $\mu_3\text{-}SO_4^{2-}$. In conclusion, in the simplified structure of LIHRIE, the sulfate anions replace 4TMP ligands as 5-connected nodes, and the triazolate ligands replace $\mu_3\text{-}SO_4^{2-}$ as 3-connected nodes. The rest three kinds of nodes are one to one correspondence with Zn1, Zn2 and μ_3-OH nodes in **5**.

Thermal analyses and X-ray powder diffraction.

To examine the thermal stabilities of all complexes, thermogravimetric analyses were carried out at a heating rate of 5°C min^{-1} under an air atmosphere. As shown in Figure 6, the TGA curves of all complexes indicate that the first weight loss occurs between 280 °C and 380 °C (355 °C for **1** and **3** ; 380 °C for **2**; 280 °C for **4**; 340 °C for **5** and **6**), corresponding to the loss of interstitial or coordinated water molecules. Simulated and experimental powder X-ray diffraction (PXRD) patterns of **2-6** are shown in Figure S2. They are in fairly good agreement with the experimental patterns, which clearly confirms the phase purity of the as-prepared products.

Luminescence Properties.

It is universally acknowledged that metal coordination frame-works with a d^{10} configuration possess excellent luminescence property.[31,32] The solid-state emission spectra of the complexes **1-6**, have been studied at room temperature, as shown in Figure 7. The emission spectra have broad peaks with maxima at 508, 468, 435, 459, 513 and 525 nm for complexes **1-6**, respectively, with the excitation upon 398 nm for **1**, 296 nm for **2**, 367 nm for **3**, 284 nm for **4**, 279 nm for **5** and 379 nm for **6.** As we know, it is usually believed that the energy transition of d^{10} complexes can be assigned as metal-to-ligand charge transfer, intraligand emission and ligand-to-metal charge transfer. In order to better understand the room-temperature fluorescent mechanism, Zheng *et al.* demonstrated that the origin of the spectral emissions observed in the spectra of the complexes can be attributed to ligand-centered charge transitions based on the 3-tzba and mixed-ligand base on the theoretical calculated results by evaluation of the density of states (DOS).[29] Based on reported literature examples, this leads us to the conclusion that the transition of Cu(I) complex **1** may be attributed to [Cu/3TPM] metal-to-ligand charge-transfer [MLCT].[30] While the photoluminescence mechanism of Zn(II) and Cd(II) complexes **2-6** is tentatively attributed to the intraligand transition of 3TMP/4TMP modified by metal coordination,[31] which also follows previous reports on analogous 5-substituted tetrazolate complexes.[32]

In comparison with the emission of coordination complexes based on Zn (complexes **2**, **4** and **5**), the emission maximums for **2** and **4** are 468 and 459 nm, which have 40-50 nm and 50-60 nm blue-shift compared to **5** (513 nm), suggesting the stronger rigidities of the frameworks of the two complexes. In addition, the maximum emission of complex **4** (459 nm) also exhibits a blue-shift compared to that of complex **2** , which may be rationalized by a stronger vibration of the free nitrate ions in framework of complex **4**, and thus resulting in more radiationless decay of the energy[25].

Complex **1** has maximum emission peak at 508 nm. Complex **3** based on 3TMP has the maximum blue-shift compared to that of **6** connected by 4TMP. The variations of photoluminescence of these complexes may be attributed to the difference of the positions of the pyridine groups, the local coordination environments of metals, and the rigidities of solid-state crystal packing.

In other words, the emission of the complexes can be adjusted *via* different positions of pyridine groups, different inorganic anions, as well as the cluster-based metal ions (seen **2**, **4**, and **5**; **3** and **6**). These emission bands in the blue region suggest that these complexes may be potential candidates as blue or green-light emitting materials.

Conclusion

In summary, six transition metal-based coordination complexes with *in situ* generated flexible ligands 3TMP/4TMP and inorganic anions (Cl^- for **2**, N_3^- for **3**, OH^- in company with NO_3^- for **4**, and OH^- in company with SO_4^{2-} for **5** and **6**), were synthesized by *in situ* tetrazole synthesis method under hydrothermal conditions. Different spatial structural features in complexes **1-6** result from subtle reaction condition changes. The inorganic anions and employed ligands also play a crucial role in the formation of complexes **1-6.** The formations of these structures provide a good example of subtle changes in the synthesis conditions that can control synthesis of the different dimension crystal structures and generate versatile tetrazole-based MOFs. From the investigation of complexes **1-6**, these complexes not only have high thermal stabilities, but also exhibit relative strong solid fluorescence intensities, which are intended for applications as photoactive materials.

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Figures and Captions

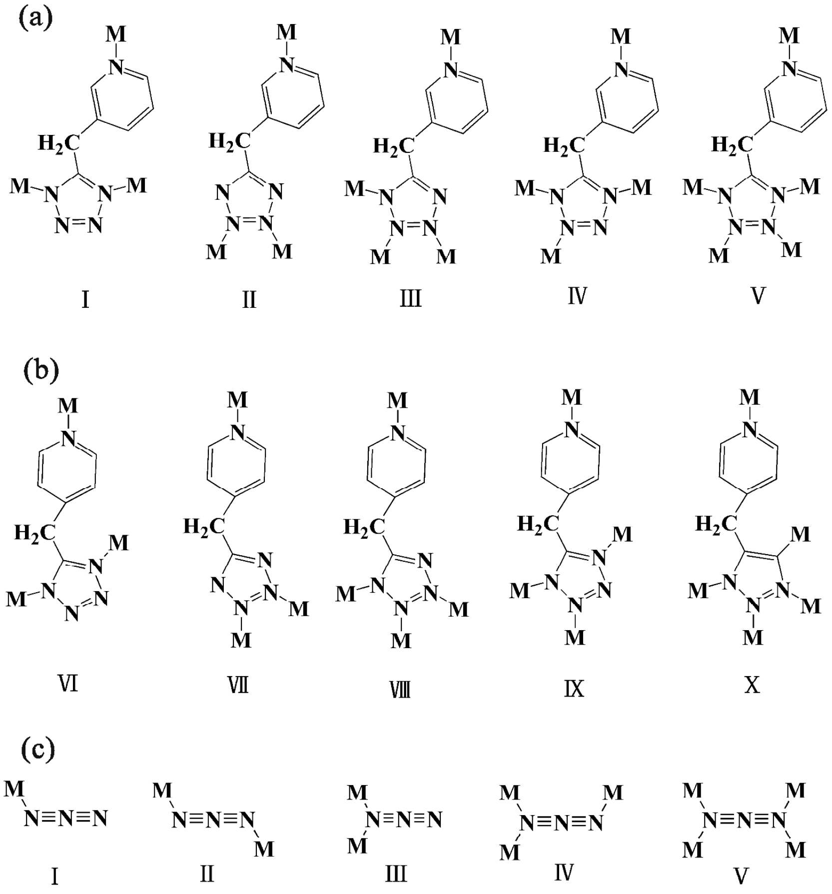
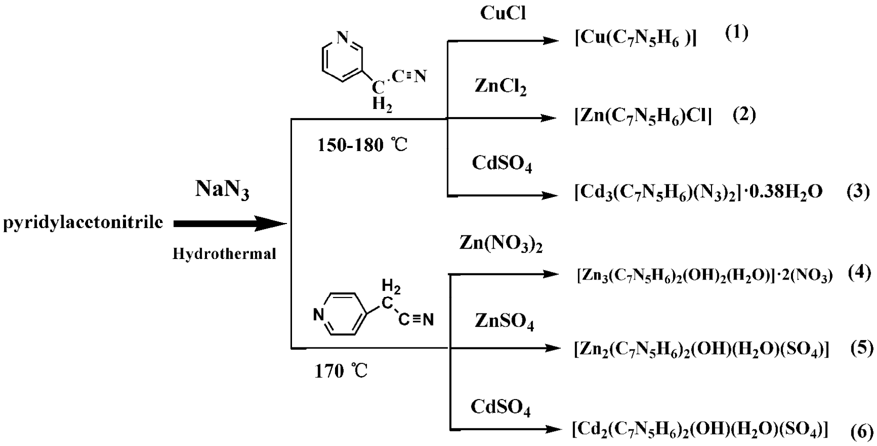


Chart 1. (a) some possible of coordination models of 3TMP. III for complex **1**, I for complex **2,** □ and III for complex **3** ; (b) some possible of coordination models of 4TMP. IX for complex **4**, X for complex **5** and **6**; (c) bridging models of N_3^-, III for N_3^- in complex **3**.



Scheme 1. Synthetic Strategy of **1-6.**

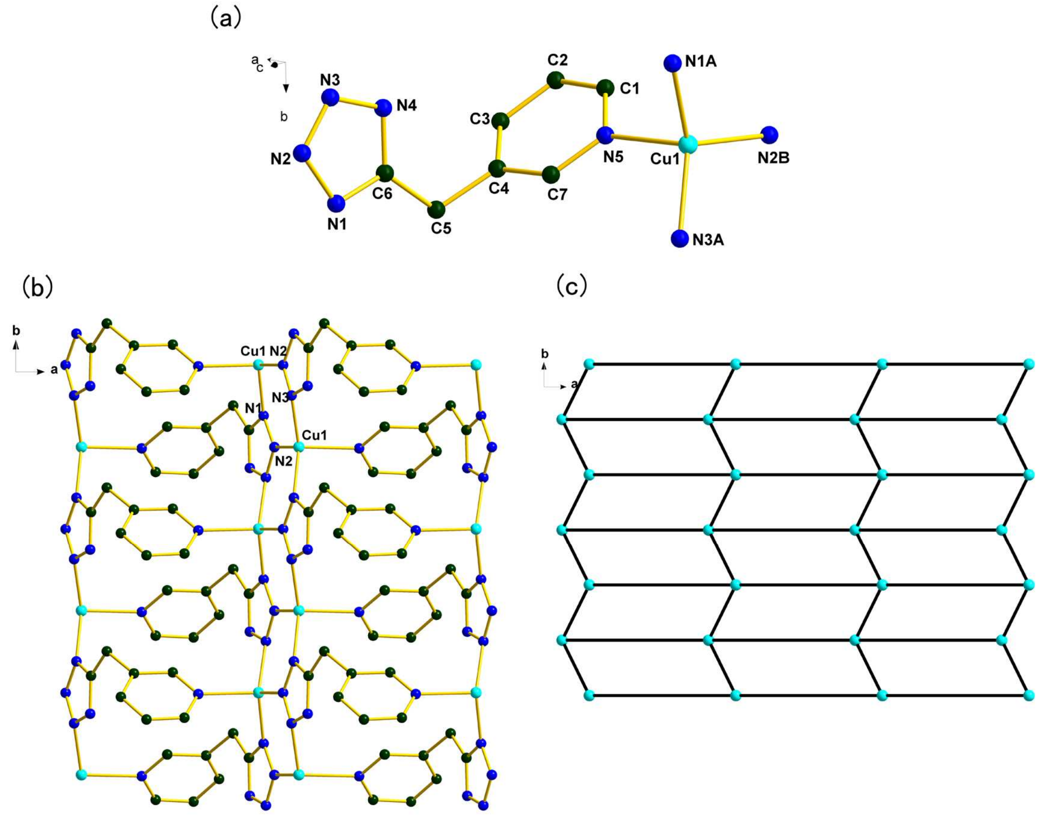


Figure 1. (a) The coordination environments of Cu atoms in **1**; **(b)** View of 2D framework along the *b*-axis of structure **1** (All H atoms were omitted for clarity). Symmetry codes: (A) –x, -0.5+y, 2-z; (B) -1+x, y, -1+z; (C) –x, 0.5+y, 2-z. **(c)** View of the **sql** net when each Cu atoms is taken as a node.

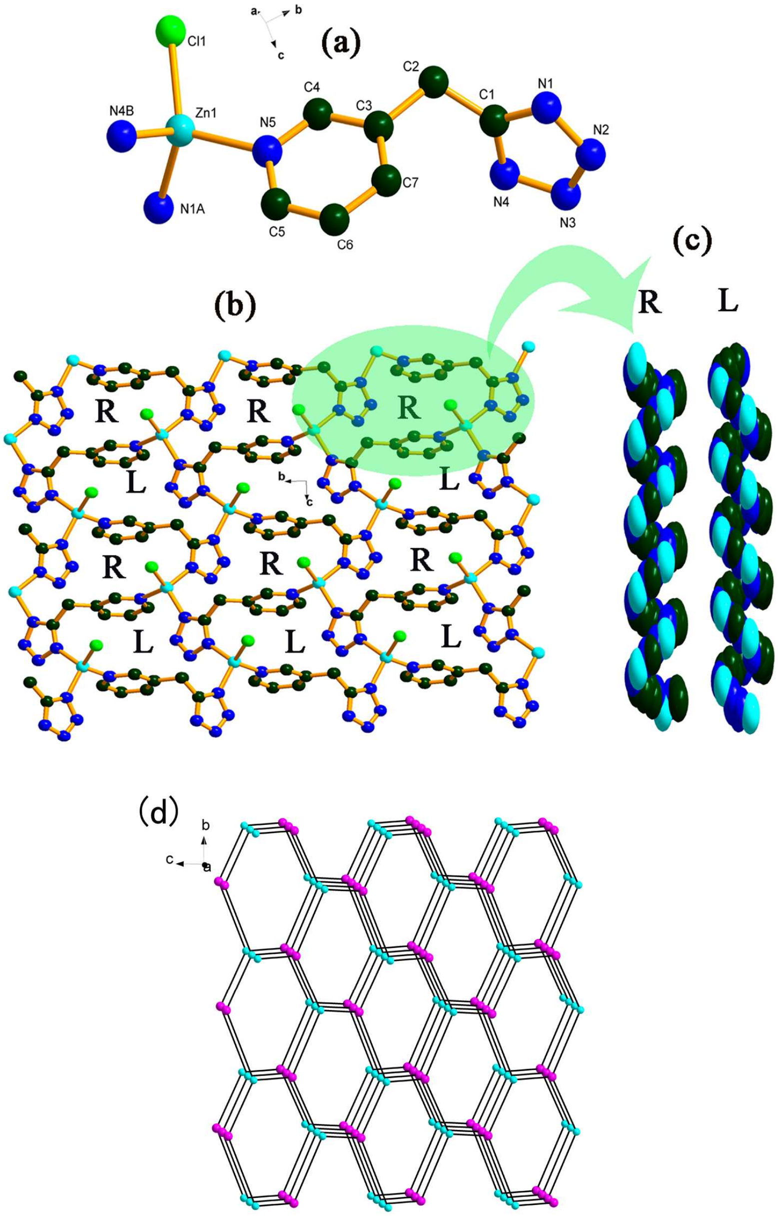


Figure 2. (a) The coordination environments of Zn atoms in **2; (b)** View of 3D coordination framework through the linkages of C1-N-Zn along the a-axis of structure **2**; **(c)** 1D helical chains are linked by Zn(□) ions and 3TMP (All H atoms were omitted for clarity). Symmetry codes: (A) 0.5+x, -0.5+y, z; (B) x, 1-y, -0.5+z. **(d)** View of the **ths** net when the Zn(II) cations and 3TMP ligands are both regarded as 3-connected nodes.

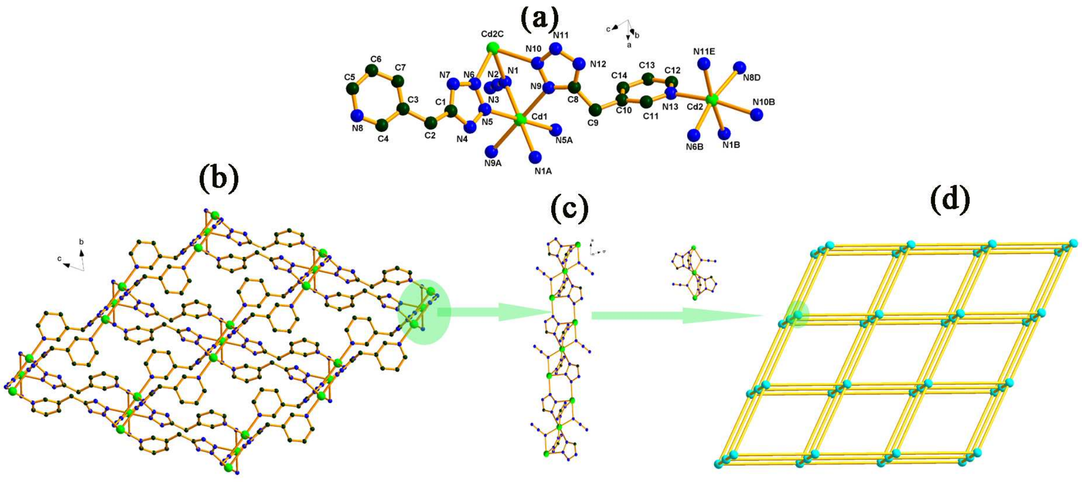


Figure 3. (a) The coordination environments of Cd atoms in **3; (b)** View of 3D coordination framework linked by the 1D chains of trinuclear [$Cd_3(N_3)_2$] building units along the a-axis of structures **3**; **(c)** 1D chain of trinuclear [$Cd_3(N_3)_2$] building unit connected by 3TMP (All H atoms and noncoordinated water molecules were omitted for clarity); **(d)** 3D 6^6 topological structure of complex **2**. Symmetry codes: (A) 2-x, -y, -z; (B) x, 1+y, -1+z; (C) x, -1+y, 1+z; (D) x, 1+y, -2+z; (E) 1-x, 1-y, -1+z.

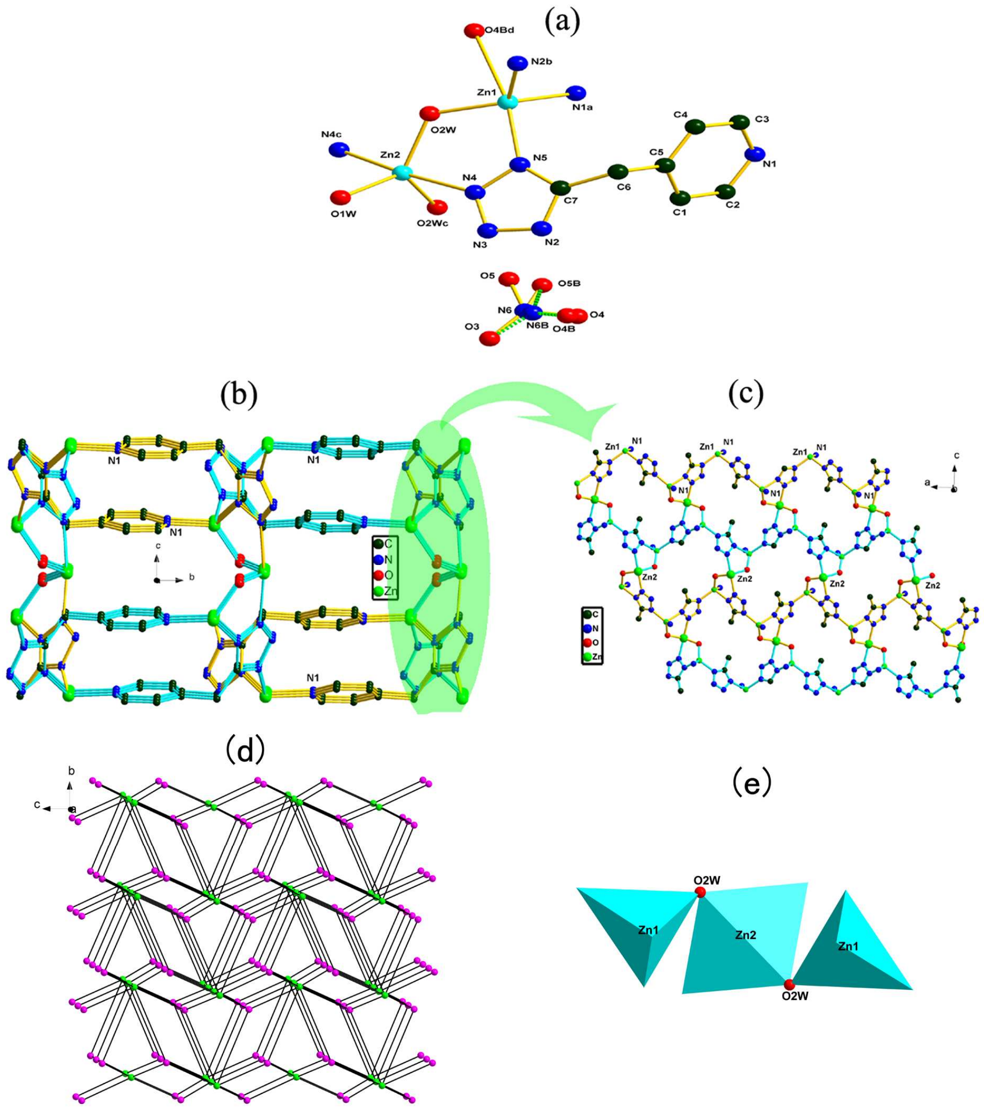


Figure 4. (a) The coordination environments of Zn atoms in **4; (b)** View of 3D MOF constructed from two-dinmensional layers and 4TMP linkers along the a-axis of structure **4**; **(c)** 2D layers networks generated from (μ_5-Zn2) and the zigzag chains linked by Zn1 and tetrazole groups of 4TMP (All H atoms were omitted for clarity). Symmetry codes: (A) 2-x, 1-y, -z; (B) 0.5+x, 0.5-y, -z; (C) 2-x, y, 0.5-z; (D) 1+x, y, z. (d) View of a binodal (3,6)-connected network with point symbol “$\{4.6^2\}2\{4^2.6^9.8^4\}$” when considering the trinuclear unit as a 6-connected node, the 4TMP ligand as a 3-connected node. (e) View of trinuclear $[Zn_3O_2]$ unit.

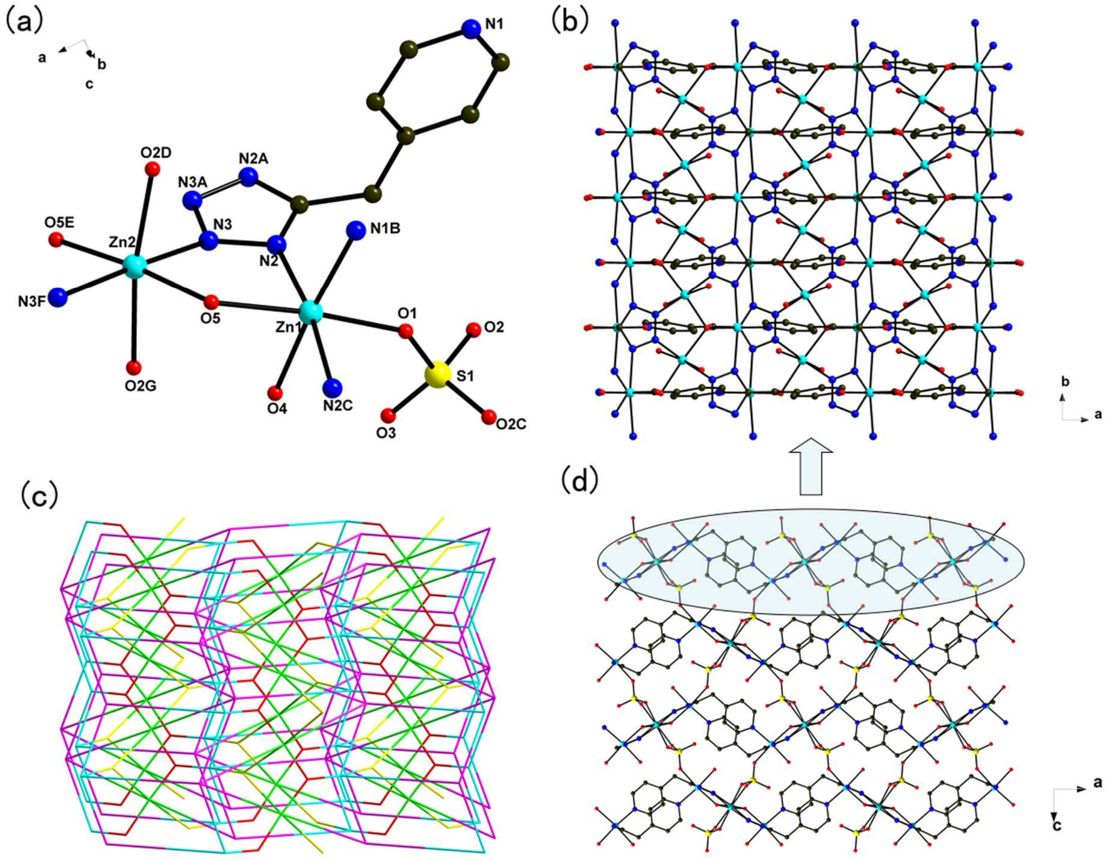


Figure 5. **(a)** The coordination environments of Zn atoms in **5; (b)** Layer substructure of **5** in the *ab*-plane. **(c)** View of the 3D (3, 3, 5, 5, 6)-connected framework with $\{4.8^2\}\{4^3\}\{4^4.6^2.8^4\}\{4^5.6^5\}\{4^8.6^6.8\}$ topolog (Zn1: blue; Zn2: green; O5: red; SO_4^{2-}: yellow; 4TMP: pink). **(d)** View of 3D MOF of structure **5**. Symmetry codes: (A) x, 0.5-y, z; (B) 1-x, 0.5+y, 1-z; (C) x, 0.5+y, 1-z; (D) 0.5-x, 1-y, -0.5+z; (E) -x, 05+y, 1-z; (F) -x, 1-y, 1-z; (G) -0.5+x, y, 0.5-z.

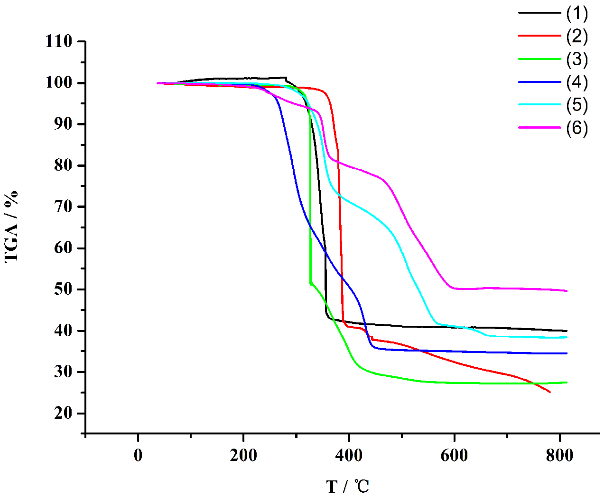


Figure 6. TG curves of complexes **1-6.**

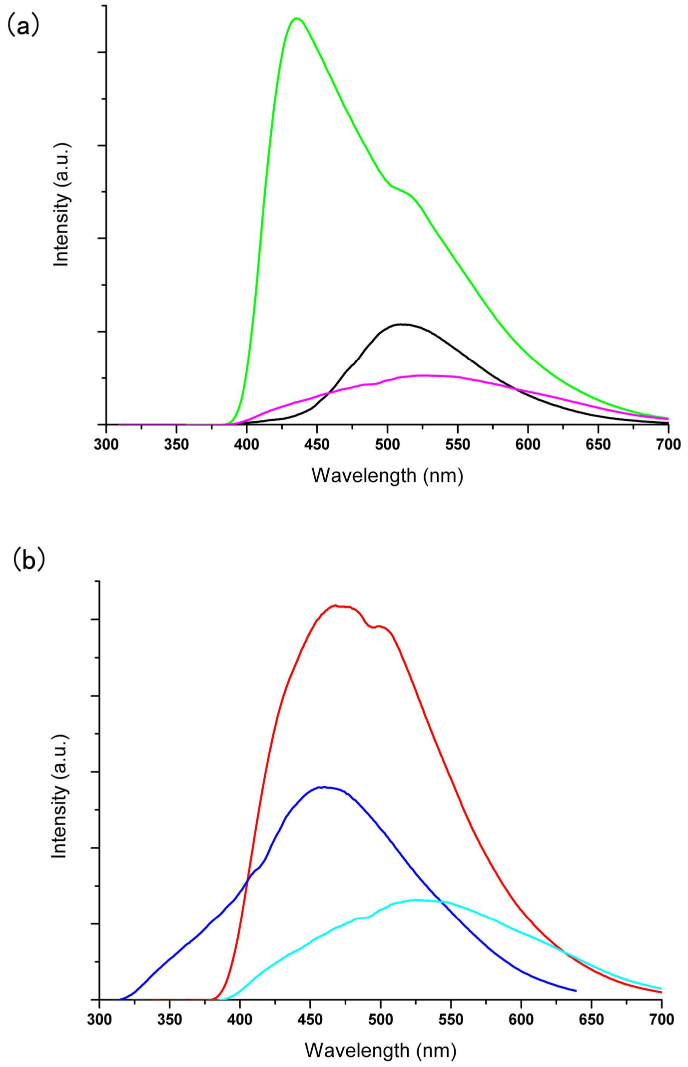


Figure 7. (a) Solid-state photoluminescence spectra of complexes **1, 3** and **6**. **1:** black; **3**: green; **6**: pink. **(b)** Solid-state photoluminescence spectra of complexes **2, 4** and **5**. **2**: red; **4**: blue; **5**: cyan.

Tables

Table 1 Crystallographic data and structure refinement summary for complexes **1–6.**

Complex	1	2	3	4	5	6
Formula	$CuC_7N_5H_6$	$ZnC_7N_5H_6Cl$	$Cd_3C_{28}N_{26}H_{24.76}O_{0.38}$	$Zn_3C_{14}N_{12}H_{16}O_9$	$Zn_2C_7N_5H_9O_6S$	$Cd_2C_7N_5H_9O_6S$
Mr	223.71	260.99	1068.77	692.50	421.99	516.05
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2(1)	Cc	P-1	Pbcn	Pnma	Pna21
a (Å)	8.394(3)	7.1396(2)	9.4625(3)	9.6478(7)	12.396(2)	12.9012(13)
b(Å)	5.7287(18)	15.8266(3)	10.8617(4)	16.0947(12)	6.7324(12)	14.0247(14)
c (Å)	9.350(3)	8.6026(2)	10.8624(4)	14.3863(11)	13.672(2)	7.0282(7)
α (°)	90	90	61.068(2)	90	90	90
β (°)	115.074(4)	100.464(1)	79.796(2)	90	90	90
γ (°)	90	90	71.950(2)	90	90	90
V ($Å^3$)	407.2(2)	955.89(4)	928.50(6)	2233.9(3)	1141.0(3)	1271.7(2)
Z	2	4	1	4	4	4
D_C(g/cm^3)	1.824	1.814	1.911	2.059	2.457	2.695
μ（mm^{-1}）	2.633	2.812	1.766	3.273	4.428	3.545
F (000)	224.0	520.0	522	1384	840	984
Goodness-of-fit	1.002	1.001	0.967	1.028	1.008	1.128
R1 [I > 2σ(I)][a]	0.0369	0.0210	0.0451	0.0289	0.0633	0.0209
wR2 (all data)[b]	0.0901	0.0433	0.1086	0.0726	0.1566	0.0506

[a] $R_1=\sum||F_0|-|F_c||/\sum|F_0|$. [b] $wR_2=\{\sum[w(F_0^2- F_c^2)^2]/ \sum w(F_0^2)^2\}^{1/2}$

Table 2. Selected Bond Distances (Å) and angles (°) for complexes **1-6**. Symmetry transformations used to generate equivalent atoms are given as footnotes.

Complex **1**

Cu(1)-N(1)#1	1.994(7)	N(1)#1-Cu(1)-N(3)#2	125.57(12)	N(2)#3-Cu(1)-N(5)	105.25(13)
Cu(1)-N(3)#2	2.019(7)	N(1)#1-Cu(1)-N(2)#3	111.7(3)	C(6)-N(1)-Cu(1)#2	132.8(5)
Cu(1)-N(2)#3	2.039(3)	N(3)#2-Cu(1)-N(2)#3	110.2(3)	N(2)-N(3)-Cu(1)#1	121.6(6)
N(2)-Cu(1)#4	2.039(3)	N(3)#2-Cu(1)-N(5)	102.7(3)	N(3)-N(2)-Cu(1)#4	125.3(6)

Complex **2**

N(1)-Zn(1)#1	2.0140(18)	C(1)-N(1)-Zn(1)#1	131.29(16)	C(1)-N(4)-Zn(1)#4	133.18(17)
N(4)-Zn(1)#4	2.0163(18)	N(5)-Zn(1)-N(1)#2	106.18(8)	N(1)#2-Zn(1)-Cl(1)	109.82(6)
Cl(1)-Zn(1)	2.1923(8)	N(1)#2-Zn(1)-N(4)#3	108.45(8)	N(5)-Zn(1)-N(1)#2	106.18(8)
N(5)-Zn(1)-N(4)#3	105.12(8)	C(1)-N(1)-Zn(1)#1	131.29(16)	C(1)-N(4)-Zn(1)#4	133.18(17)

Complex **3**

Cd(1)-N(1)#1	2.284(5)	Cd(2)-N(11)#2	2.310(4)	Cd(2)-N(10)#3	2.498(4)
N(10)-Cd(2)#5	2.498(4)	N(8)-Cd(2)#6	2.355(5)	C(5)-N(8)-Cd(2)#6	126.6(4)
N(8)-Cd(2)#4	2.355(5)	N(11)#2-Cd(2)-N(6)#3	97.82(16)	N(5)-N(6)-Cd(2)#5	119.1(3)
N(1)-Cd(1)-N(1)#1	180.0	N(6)#3-Cd(2)-N(8)#4	168.19(15)	N(1)#3-Cd(2)-N(8)#4	88.55(16)

Complex **4**

N(1)-Zn(1)#1	2.001(3)	N(5)-Zn(1)	2.091(2)	N(6)-O(3)	1.217(12)
N(4)-Zn(2)	2.214(2)	N(6)-O(4)	1.239(12)	N(6)-O(5)	1.213(12)

N(2)-Zn(1)#2	2.001(2)	O(1W)-Zn(2)	1.969(3)	O(2W)-Zn(1)	1.8954(18)
O(2W)-Zn(2)	1.9552(18)	Zn(1)-N(2)#3	2.001(2)	Zn(2)-N(4)#4	2.214(2)
C(7)-N(2)-Zn(1)#2	132.75(17)	N(3)-N(2)-Zn(1)#2	118.68(15)	N(3)-N(4)-Zn(2)	128.33(16)
N(5)-N(4)-Zn(2)	120.08(15)	C(7)-N(5)-Zn(1)	139.80(16)	N(4)-N(5)-Zn(1)	114.79(15)
O(3)-N(6)-O(4)	118.3(11)	O(3)-N(6)-O(5)	121.1(11)	O(4)-N(6)-O(5)	120.5(11)
O(2W)-Zn(1)-N(1)#1	123.53(9)	O(2W)-Zn(1)-N(2)#3	117.45(9)	N(1)#1-Zn(1)-N(2)#3	108.99(9)
O(2W)-Zn(1)-N(5)	93.33(8)	N(1)#1-Zn(1)-N(5)	104.46(8)	N(2)#3-Zn(1)-N(5)	104.78(8)
O(2W)-Zn(2)-N(4)#4	90.10(8)	O(2W)#4-Zn(2)-N(4)#4	86.07(7)	O(1W)-Zn(2)-N(4)	93.78(5)

Complex **5**

Zn(1)-N(1)#1	2.118(9)	Zn(1)-N(2)	2.274(6)	Zn(1)-N(2)#2	2.274(6)
Zn(1)-O(5)	2.140(7)	Zn(1)-O(1)	2.128(7)	Zn(1)-O(4)	2.084(8)
Zn(2)-O(5)	2.061(4)	Zn(2)-O(5)#3	2.061(4)	Zn(2)-O(2)#4	2.171(6)
Zn(2)-N(3)#3	2.122(6)	Zn(2)-N(3)	2.122(6)	Zn(2)-O(2)#5	2.171(6)
N(1)-Zn(1)#1	2.118(9)	O(2)-S(1)#2	1.467(7)	O(3)-S(1)#2	1.463(10)
O(2)-Zn(2)#6	2.171(6)	O(5)-Zn(2)#7	2.061(4)	O(1)-S(1)	1.474(7)
O(2)-S(1)	1.467(7)	O(3)-S(1)	1.463(10)	O(4)-Zn(1)-N(2)	86.80(16)
O(4)-Zn(1)-O(5)	173.3(4)	N(1)#1-Zn(1)-O(1)	88.4(3)	O(5)-Zn(1)-O(1)	173.7(3)
O(5)-Zn(1)-N(1)#1	173.9(11)	O(1)-Zn(1)-O(5)	173.7(3)	N(3)-Zn(2)-O(3)#5	91.2(3)
O(5)-Zn(2)-O(2)#5	88.2(3)	O(5)#3-Zn(2)-O(2)#5	91.8(3)	O(6)#3-Zn(2)-N(3)#3	92.4(2)
O(2)#4-Zn(2)-N(3)	91.2(3)	N(3)-Zn(2)-N(3)#3	180.000(1)	S(1)-O(1)-Zn(1)	142.4(5)
O(3)-S(1)-O(1)	109.7(5)	O(4)-S(1)-O(2)	122.7(6)	O(1)-S(1)-O(2)	108.2(3)

complex **6**

Cd(1)-O(1)	2.248(2)	Cd(1)-O(6)	2.284(2)	Cd(1)-O(5)	2.309(2)
Cd(1)-N(1)#1	2.310(3)	Cd(1)-N(2)#2	2.449(4)	Cd(2)-O(6)#3	2.235(3)
Cd(2)-O(2)#4	2.251(3)	Cd(2)-O(6)	2.236(4)	Cd(2)-O(3)#5	2.357(3)
N(1)-Cd(1)#6	2.310(3)	Cd(1)-N(3)	2.400(4)	N(2)-Cd(1)#7	2.449(4)
N(5)-Cd(2)#8	2.333(3)	O(2)-Cd(2)#9	2.251(3)	O(3)-Cd(2)#10	2.357(3)
O(1)-S(1)	1.472(2)	O(2)-S(1)	1.481(3)	O(3)-S(1)	1.480(3)
O(4)-S(1)	1.457(3)	O(1)-Cd(1)-O(5)	86.91(9)	O(6)-Cd(1)-O(5)	90.85(8)
O(1)-Cd(1)-N(1)#1	86.75(9)	O(5)-Cd(1)-N(1)#1	173.13(10)	O(1)-Cd(1)-N(3)	92.99(12)
O(6)-Cd(1)-N(3)	85.92(12)	O(5)-Cd(1)-N(3)	83.88(13)	N(1)#1-Cd(1)-N(3)	99.07(14)
O(1)-Cd(1)-N(2)#2	89.66(11)	O(6)-Cd(1)-N(2)#2	90.98(12)	O(5)-Cd(1)-N(2)#2	84.48(13)
N(3)-Cd(1)-N(2)#2	167.90(9)	O(6)#3-Cd(2)-O(6)	169.38(8)	O(6)-Cd(2)-O(2)#4	84.54(11)
O(6)-Cd(2)-N(5)#3	94.16(11)	O(6)-Cd(2)-O(3)#5	84.09(9)	Cd(2)#8-O(6)-Cd(2)	104.46(10)
Cd(2)#8-O(6)-Cd(1)	118.39(13)	Cd(2)-O(6)-Cd(1)	115.41(14)	O(4)-S(1)-O(1)	111.31(16)
O(4)-S(1)-O(3)	110.8(2)	O(1)-S(1)-O(3	106.69(16)	O(4)-S(1)-O(2)	111.1(2)
O(1)-S(1)-O(2)	107.67(19)	O(3)-S(1)-O(2)	109.08(18)		

Symmetry codes for **1:** #1 -x,y-1/2,-z+2 **;** #2 -x,y+1/2,-z+2; #3 x-1,y,z-1; #4 x+1,y,z+1. **2:** #1 x-1/2,y+1/2,z; #2 x+1/2,y-1/2,z; #3 x,-y+1,z-1/2; #4 x,-y+1,z+1/2. **3:** #1 -x+2,-y,-z; #2 -x+1,-y+1,-z-1; #3 x,y+1,z-1; #4 x,y+1,z-2; #5 x,y-1,z+1; #6 x,y-1,z+2. **4:** #1 -x+2,-y+1,-z; #2 x-1/2,-y+1/2,-z; #3 x+1/2,-y+1/2,-z; #4 -x+2,y,-z+1/2. **5:** #1 -x+1,-y+1,-z+1; #2 x,3/2-y,z; #3 -x,-y+1,z+1; #4 x-1/2,y-,z+1/2; #5 -x+1/2,-y+1,z+1/2; #6 -x+1/2,-y+1,z-1/2; #7 -x,y+1,-z+1; #8 x,-y+1/2,z. **6:** #1 -x+1,-y+2,z+1/2; #2 x,y,z+1#3 –x,-y+2,z+1/2; #4 -x+1/2,y+1/2,z+1/2; #5 x-1/2,-y+3/2,z; #6 -x+1,-y+2,z-1/2; #7 x,y,z-1; #8 –x,-y+2,z-1/2; #9 -x+1/2,y-1/2,z-1/2; # 10 x+1/2, -y+3/2, z.

Table 3. Hydrogen Bonds of Complexes 2-6.

D—H…A	d(D—H) (Å)	D(H…A) (Å)	d(D…A) (Å)	∠(D—H…A) (deg)
Complex **2**				
C(7)—H(7)…Cl(1)	0.93	2.82	3.516(3)	133
Complex **3**				
C(7)—H(7)…N(1)	0.93	2.40	3.033(8)	125
C(12)—H(12)…N(3)	0.93	2.54	3.352(11)	147
Complex **4**				
O(1W)—H(1W)…O(4B)	0.81(3)	2.58(3)	3.115(7)	126(3)
O(1W)—H(1W)…O(5B)	0.81(3)	1.93	2.731(4)	171(4)
O(2W)—H(2W)…O(3)	0.79(3)	2.08(3)	2.868	176(3)
O(2W)—H(2W)…O(4B)	0.79(3)	2.44(3)	2.940(6)	122(2)
C(3)—H(3)…0(3)	0.93	2.54	3.416(3)	158
C(6)—H(6B)…0(3)	0.97	2.56	3.142(3)	119
Complex **5**				
O(4)—H(1W)…O(2)	0.82(4)	2.37(8)	3.034(10)	139(7)
O(4)—H(1W)…O(3)	0.81(3)	2.25(13)	2.715(13)	117(14)
O(5)—H(5A)…O(2)	0.98	2.52	2.946(8)	106
C(1)—H(1)…O(1)	0.93	2.24	2.887(14)	126
C(2)—H(2)…O(3)	0.93	2.23	3.118(15)	159

C(5)—H(5B)…O(3)	0.96	2.53	2.982(19)	109
C(6)—H(6A)…O(2)	0.97	2.40	3.338(10)	162
C(6)—H(6B)…O(2)	0.97	2.40	3.338(10)	162
		Complex **6**		
O(5)—H(1A)…O(3)	0.85	2.12	2.819(4)	139
O(5)—H(1B)…O(4)	0.87	1.92	2.737(4)	156
C(2)—H(2)…O(1)	0.93	2.41	3.060(5)	127
C(6)—H(6D)…O(2)	0.97	2.50	3.429(7)	160