Reversible shrinkage and expansion of a blue photofluorescent cadmium coordination polymer and *in situ* tetrazole ligand synthesis†

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The metal–organic framework $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4]$ (5-MT = 5-methyl-1H-tetrazole) with an unprecedented $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ core and two kinds of tetrazole coordination modes was formed by self-assembly and *in situ* synthesis of the 5-MT tetrazole ligand; the structure exhibits an unusual $3^9{\cdot}4^{12}{\cdot}5^{15}$ topological network and shows reversible shrinkage and expansion in a crystal-to-crystal dehydration/rehydration process.

The design, synthesis, characterization and properties of supramolecular architectures are, owing to their intriguing network topologies and potential applications in storage, catalysis, molecular magnets, recognition and photoluminescence, of great interest to researchers in many areas of materials science.[1,2] Types of ligands that can be used to form such supramolecular assemblies are tetrazoles, and the literature on tetrazolates and their complexes is expanding rapidly and these compounds play an important and growing role in coordination chemistry, medicinal chemistry, and especially materials science.[3] Recently, a new facile approach was developed to synthesize 5-substituted 1H-tetrazoles.[4] In the general reaction, tetrazoles are prepared through a [2 + 3] cycloaddition reaction of an azide and nitriles in water with the aid of a Lewis acid such as a zinc salt. So far, most of the work in the field of constructing tetrazole coordination frameworks has been done by varying the metal ions and especially Zn^{II}, Cd^{II}, Co^{II}, Fe^{II}, Cu^{I}/Cu^{II}, and Ag^{I} have been used extensively.[5–7] Tetrazolates have a large range of possible coordination geometries—the most prevalent being complexes in which the tetrazolates act as mono- and bidentate ligands[8]—and have the ability to form various types of coordination networks that exhibit a wide range of different topological architectures. However, the actual role of the transition metal ions in the formation of the networks is still unclear, and it still remains challenging to rationally control the synthesis of tetrazole coordination polymers with specific novel structural motifs and properties. Recently, Xiong and Li and co-workers studied the self-assembly of suitable tetrazolates *via in situ* ligand synthesis, and they isolated a series of coordination polymers with intriguing structural motifs and luminescent properties.[5,6] Further research, however, is needed in this field, and we report here a novel cubic and highly photoluminescent tetrazolate coordination framework generated by *in situ* synthesis of 5-methyl-1H-tetrazole (5MT) as the ligand. Simple hydrothermal reaction of cadmium sulfate with azide in an acetonitrile–water mixture (v/v 1 : 1) at 150 °C (50 h) led to the formation of cubic colourless **1** in a reasonably high yield.‡

X-Ray single-crystal structural analysis of **1** revealed that it crystallizes in the cubic space group *I*-43*d*, and is composed of a three-dimensional framework with an unprecedented $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)^{3+}$ core as the central building block with each cadmium atom being coordinated to the central μ_3-OH and the μ_3-SO_4 groups. The core unit is, in turn, surrounded by $Cd(5MT)_6^{\ 4-}$ units. The 5-methyl-1H-tetrazole ligands were obviously *in situ* generated from the starting materials, azide anions and acetonitrile, *via* a [2 + 3] dipolar cycloaddition reaction (Scheme 1). The structure of **1** thus exhibits two crystallographically independent cadmium atoms, those in the $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)^{3+}$ and in the $Cd(5MT)_6^{\ 4-}$ units, and two types of tetrazole ligands: one that is disordered across a twofold axis and coordinates to three metal atoms, and a second coordinated to four metal atoms. Cd1 of the $Cd(5MT)_6^{\ 4-}$ units lies at a site with −4 symmetry and is coordinated by six nitrogen atoms from six different 5MT ligands in a slightly distorted octahedral coordination environment. The bond lengths range from 2.339(3) to 2.351(2) Å. Cd2 of the $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)^{3+}$ is located on a general position, defined by four nitrogen atoms from four 5MT ligands [Cd–N = 2.349(2)–2.415(2) Å], and two oxygen atoms from the μ_3-OH and the sulfate groups [Cd–O = 2.279(2) and 2.263(1) Å], respectively.

The structure of **1** may be described in terms of the interconnected $Cd_3(L)_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ subunits. One such subunit is shown in Fig. 1. They consist of three Cd metal atoms which lie at the corners of an equilateral triangle. Each set of two Cd atoms is bridged on the sides by one type of 5MT ligand, and all three are connected with each other in the middle by a μ_3-OH anion (which lies 0.76 Å below the plane of the metal atoms), and straddled on the top by a μ_3-SO_4 anion. A threefold axis passes through this subunit, such that the hydroxide and sulfate anions lie on it, and the three Cd2 atoms and three 5MT ligands are related to each other by this axis. Each subunit is connected to nine others *via* both types of

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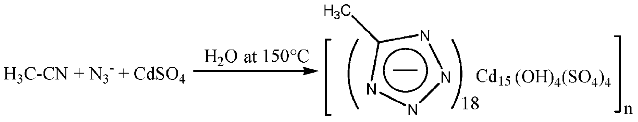
† Electronic supplementary information (ESI) available: Crystallographic data for compounds **1–4** in CIF format (CCDC 674092–674095), IR spectra, TG, fluorescence spectra, power X-ray diffraction plots and additional figures. See DOI: 10.1039/b800938d



Scheme 1 *In situ* hydrothermal synthesis of **1**.

bridging 5MT ligands from three $Cd(5MT)_6^{4-}$ units, as shown in Fig. 2, thus forming a complicated 3D network structure that also involves interstitial water molecules.

If the $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)^{3+}$ subunits are taken as nodes of a topological network, a complicated nine-connected architecture is generated (see ESI, Fig. S1†) in which the subunit nodes are connected *via* the bridging tetrazole ligands and the Cd1 atoms. The topology of this network is $3^9{\cdot}4^{12}{\cdot}5^{15}$. The structure can also be described as a 3,4-connected C_3N_4 (ctn) net $[(8^3)_4(8^6)_3]$, where the trimer is the 3-connecting node and Cd1 is the 4-connecting node (Fig. 3), however this description ignores the fact that the 5MT bridges connect more than two nodes each.

The single-crystal analysis for compound **1** placed the number of interstitial water molecules at 8.5 per asymmetric unit. A Platon analysis found no solvent accessible voids upon removal of the water molecules from the structure,[9] and all points in the space vacated have a distance of less than 0.8 Å from the next van der Waals surface. TGA analysis of **1** (see ESI, Fig. S2†) indicates that **1**, while being otherwise stable up to 383 °C, loses about 3.92% of its weight in the range 180–255 °C (loss of all the interstitial water molecules would amount to a weight decrease of 4.0%). Decomposition of the 5MT ligands occurs in the range of 383 °C to 424 °C. To get a better understanding of the properties of the interstitial water molecules, the de- and rehydration behaviour of **1** was analyzed in more detail by single-crystal X-ray diffraction at different temperatures. X-Ray analysis of single crystals heated to 200 °C under vacuum for 3 h revealed that interstitial water molecules in the structure were completely removed and yielded a final composition of $([Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4{\cdot}2.32H_2O]$ for **2** (see ESI†). The partial dehydration is accompanied by a slight decrease in volume of 130.8 Å^3 (from 9936.0 to 9805.2 Å^3). Further heating of the single crystals at 300 °C under vacuum for 3 h yielded totally dehydrated $[Cd_{15}(5MT)_{18}(OH)_4(SO_4)_4]$ (**3**) (see ESI†). The complete removal of all interstitial water molecules is accompanied by an additional slight decrease in volume by 92.7 Å^3 (from 9805.2 to 9712.5 Å^3). The decrease in cell volume upon removal of the guest water molecules is similar to what has been observed in other framework materials.[10] The molecular frameworks in **2** and **3** are basically unchanged when compared with **1**, and the average Cd–O to N distances are almost identical. When the crystals of **3** were immersed in water for one day the original composition of was largely re-established with 7.99 molecules of water per asymmetric unit and the volume was determined to be 9955.8 Å^3, demonstrating a completely reversible shrinkage and expansion.

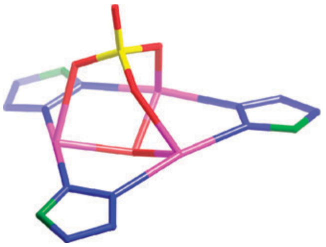


Fig. 1 A view of the $Cd_3(5MT)_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ subunit. For clarity CH_3 groups and H atoms are not shown. N atoms are represented as blue, C green, Cd2 pink, O red, and S yellow.

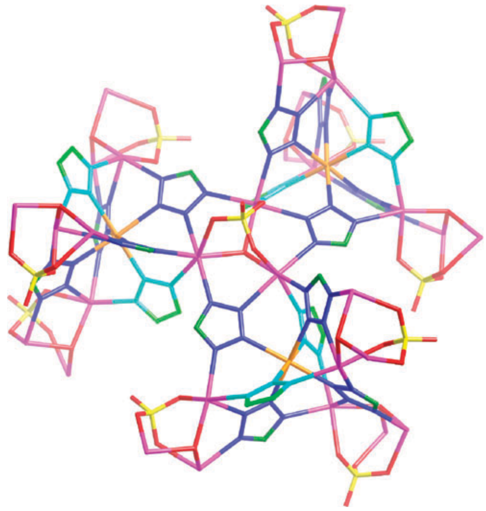


Fig. 2 The connection of one $Cd_3(L)_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ subunit to nine others *via* three $Cd(5MT)_6$ units. For clarity the two types of tetrazole ligands are shaded differently (dark and light blue), as are the Cd atoms (Cd1: orange; Cd2: pink), H atoms and CH_3 groups are omitted; peripheral subunits are represented just by their $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ cores.

The fluorescence of the as-synthesized compound **1** was studied in the solid state at room temperature (see ESI, Fig. S3†) and a relatively intense blue emission at about 401 nm was observed (λ_{ex} 349 nm) that may be ascribed to the cooperative effects of intraligand emission and ligand-to-metal charge transfer (LMCT).[11]

In summary, we have successfully isolated a novel coordination polymer with an unprecedented $Cd_3(\mu_3\text{-}OH)(\mu_3\text{-}SO_4)$ core through *in situ* tetrazole ligand synthesis, which exhibits an

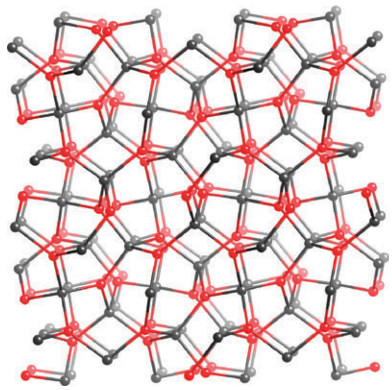


Fig. 3 Schematic representation of the alternative 3,4-connecting C3N4 net description of **1**, where the 3-connecting nodes (red spheres) are the Cd2 trimers and the 4-connecting nodes (grey) are the Cd1 atoms.

unusual topological network and shows reversible shrinkage and expansion in a single-crystal-to-single-crystal dehydration/rehydration process.

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Notes and references

‡ A mixture of $CdSO_4 \cdot 8H_2O$ (0.352 g; 1 mmol), NaN_3 (0.065 g; 1 mmol), CH_3CN (3 mL) and H_2O (3 mL) was sealed in a 15 mL Teflon-lined reactor, which was heated in an oven to 150 °C for 50 h, then cooled to room temperature at a rate of 5 °C h^{-1}. Colourless cubic crystals were obtained in 35% yield, based on Cd. Elemental analysis (%) calcd for **1** ($C_{36}H_{75}Cd_{15}N_{72}O_{28.5}S_4$), C, 11.42; H, 2.00; N, 26.63; S, 3.39. Found: C, 11.50; H, 2.09, N, 26.56; S, 3.36. IR (KBr, cm^{-1}): 3462, 1643, 1579, 1487, 1436, 1373, 1263, 1182, 1166, 1058, 983, 694, 617, 457. **Warning: sodium azide is potentially explosive under the hydrothermal reaction conditions.** Other detailed synthetic procedures, additional figures and TG plots can be found in the ESI†.
All crystallographic measurements were made on a Bruker SMART APEX II CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) operated at 2000 W power (50 kV, 30 mA). The structure was solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL software suite. All non-hydrogen atoms were refined anisotropically. Crystallographic data for compound **1**: cubic *I*-43*d*, with $a = 21.4983(1)$ Å, $V = 9936.02(8)$ Å^3, $Z = 4$, μ(Mo Kα) = 3.326 mm^{-1}, $\rho = 2.532$ g cm^{-3}, $T = 296$ K, R_1 [$I > 2\sigma(I)$] = 0.0144 and $wR2$ (all data) = 0.0366, GOF = 1.210. Data of compounds **2**–**4** can be found in the ESI†.

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