

Synthesis, crystal structure and properties of a 3D zinc(II) coordination polymer with asymmetric 3-amino-1,2,4-triazolate

Wen Tao Fan, Jiao Jiao Du, Quan Qing Xu, Jun Feng Kou* & Feng Yi Liu*

College of Chemistry and Chemical Engineering Yunnan Normal University, Kunming, Yunnan, 650 500, PR China

Email: kjf416@163.com (JFK)/ lfy20110407@163.com (FYL)

Received 4 May 2018; revised and accepted 27 July 2018

A new coordination polymer, $[\text{Zn}_2\text{SO}_4(\text{atz})_2(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})_4$ (**1**) (Hatz = 1H-3-amino-1,2,4-triazole) has been synthesized using zinc sulfate and an asymmetric 3-substituted triazole ligand at room temperature. X-ray analysis reveals that complex **1** shows a 3D-framework containing $\text{Zn}_2(\text{atz})_2(\text{H}_2\text{O})_2\text{SO}_4$ subunits, which display a 6-coordinated unimodal pcu topological network. Further, complex **1** exhibits purple fluorescence with an emission maximum at 405 nm in the solid state at room temperature.

Keywords: Coordination polymers, 3D-Framework, X-ray structure, Fluorescence, Zinc sulfate, Triazoles, Symmetric triazoles

Metal-organic frameworks (MOFs) are considered as promising candidates with potential applications because of their intriguing topologies and structural tunability¹. However, most of the design and construction of the desired MOFs depend on the nature of the organic ligands. The architectures and functionality of MOFs are strongly influenced by the flexibility, length, coordination ability and symmetry of the organic ligands^{2,3}.

Nowadays, metal-azolate frameworks (MAFs) are of increasing interest among the crystal engineering community due to the diversity of novel structures that can be designed⁴, and the richness of properties that can be expected. Among these, 1,2,4-triazoles (Htaz) and their derivatives have proved to be rather useful in the construction of MOFs due to their versatile coordination modes and metal-binding conformations. Moreover, polynuclear metal-triazolato clusters usually function as secondary building units (SBUs) in MOFs and therefore are multi-connected nodes⁵. Nevertheless, current researches have focused mainly on symmetrically

substituted triazolate ligands⁶, and metal complexes of asymmetric triazoles have few reports⁷⁻¹⁰.

We have noted that introduction of coordinating anions dramatically influences the structures and properties of the composite materials. The structural influences are most pronounced when the anion is sulfate¹¹, but till recently reports on sulfate-pillared MOF materials were rare¹²⁻¹⁴. Similar to both pyrazole and imidazole ligands, triazolyl ligands can be considered as a representative hybrid of both pyrazole and imidazole³. Zinc(II) being rather flexible in its coordination geometries and coordination numbers, it is expected that there will be a rich structural diversity when Zn(II) is combined with 1,2,4-triazolates¹⁵. Chen *et al.*¹⁶ constructed the SOD- $[\text{Zn}(\text{mtz})_2]$ (MAF-7) that is isostructural with MAF-4. Zubieta *et al.*^{17,18} reported a variety of M/triazolate/X ternary metal triazolate frameworks (M = Cu (I, II), Zn(II), and Cd(II); X = F⁻, Cl⁻, Br⁻, I⁻, OH⁻, SO₄²⁻, and NO₃⁻), in which the metal ions show various types of common coordination geometries. Lin *et al.*¹⁴ have reported a pcu-like network of the zinc(II)/ATRZ layers pillared by the inorganic sulfates¹⁴.

Encouraged by these results, we investigated the complex structure of zinc sulfate with the asymmetric Hatz ligand¹⁹⁻²³ to further study how the substituent group and coordination anion impact the structures of metal-triazolate framework. Herein, we report a new 3D zinc(II) coordination polymer with asymmetric 3-amino-1,2,4-triazolate prepared at room temperature.

Experimental

The ligand, Hatz, was purchased from J&K Scientific Ltd, China. Other reagents and solvents were commercially available and were used without further purification. IR spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FTIR spectrometer in the 400–4000 cm⁻¹ region. Elemental analysis (C, H, N) was performed on a Perkin-Elmer 240 elemental analyzer. Fluorescent spectra were performed on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp and a F900 microsecond flash lamp.

For the synthesis of $\text{Zn}_2\text{SO}_4(\text{atz})_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$ (**1**), a solution of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (287.6 mg, 0.1 mol) in 4 mL of water was mixed with 4 mL of an absolute

ethanol solution of 1H-3-amino-1,2,4-triazole (84.1 mg, 0.1 mol). The resulting mixture was allowed to evaporate for three days to yield colorless block-shaped crystals and then filtered, washed with water, and dried in air to afford 20.0 mg of the product (Yield: 80% based on Hatz). Similar to an earlier procedure, base was not used for the reaction. For $C_4H_{18}N_8O_{10}SZn_2$ Calcd: (%) C 9.59; H 3.62; N 22.36. Found: C 9.57; H 3.60; N 22.33%. IR (KBr; ν , cm^{-1}): $\nu = 3420$ w, 1625 s, 1556 s, 1400 s, 1306 w, 1113 s, 620 s, 484 m (Supplementary data, Fig. S1).

Crystallographic data of **1** were collected at room temperature on a Bruker Apex CCD diffractometer with graphite-monochromate Mo-K α radiation ($= 0.71073 \text{ \AA}$). Absorption correction was applied using the multi-scan program SADABS²⁴. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package²⁵. Anisotropic thermal parameters were applied to all non-hydrogen atoms. H atoms attached to C atoms were constrained with C-H = 0.96 \AA and $U_{iso}(\text{H}) = 1.5 U_{eq}(\text{C})$. N-bonded H atoms were constrained with N-H = 0.86 \AA and $U_{iso}(\text{H}) = 1.2 U_{eq}(\text{N})$. Water H atoms were located from a different Fourier map and restrained with O-H = 0.820(11) \AA and $U_{iso}(\text{H}) = 1.5 U_{eq}(\text{O})$. Crystal data as well as details of data collection and refinement for complex **1** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Results and discussion

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the orthorhombic space group $Pnma$, and exhibits a 3D porous metal-organic framework containing $Zn_2(\text{atz})_2(\text{H}_2\text{O})_2\text{SO}_4$ subunits, which is different from $Zn_2(\text{atz})_2\text{SO}_4$ ¹⁴. In the asymmetric unit of complex **1**, there is one independent Zn ion, half an atz, one coordinated water molecule, three free water molecules, one μ_2 -O coordinated sulfate anion (lying on a twofold axis) and two N atom (N^1 , N^2) from the two triazolyl groups of two different atz ligands. As shown in Fig. 1, each Zn atom is present in a five-coordinate N_3O_2 environment. The coordination geometry of the metal center is best described as distorted trigonal bipyramid with the Zn atom located slightly above the centre of the triangle defined by the three triazolyl N atoms. The bond lengths of Zn-N1, Zn-N2, Zn-N3, Zn-O1W and Zn-O2 (SO_4^{2-}) are 1.989(6), 1.997(6), 1.993(6), 2.421(6) and 2.147(5) \AA , respectively. The Zn-O1W(water) bond distance is obviously longer

Table 1 — Crystal data and structure refinement of **1**

| | |
|--|--|
| Formula | $C_4H_{10}N_8O_6SZn_2 \cdot 4(\text{H}_2\text{O})$ |
| Crystal system, | Orthorhombic |
| Space group | $Pnma$ |
| Temperature, K | 293 |
| a (\AA) | 10.441 (2) |
| b (\AA) | 15.283 (3) |
| c (\AA) | 10.235 (2) |
| V (\AA^3) | 1633.2 (5) |
| Z | 4 |
| Radiation type | Mo-K α |
| μ (mm^{-1}) | 3.13 |
| Crystal size (mm) | 0.28 \times 0.25 \times 0.23 |
| T_{min} , T_{max} | 0.433, 0.486 |
| No. of measured | 10611 |
| No. of independent | 1429 |
| No. of obs. [$I > 2\sigma(I)$] reflections | 924 |
| R_{int} | 0.140 |
| $(\sin \theta/\lambda)_{max}$ (\AA^{-1}) | 0.595 |
| $R[F^2 > 2\sigma(F^2)]$ | 0.068 |
| $wR(F^2)$ | 0.175 |
| S | 1.03 |
| No. of Reflections | 1429 |
| No. of parameters | 141 |
| No. of restraints | 12 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ ($e \text{ \AA}^{-3}$) | 0.78, -0.64 |

Table 2 — Selected bond lengths (\AA) and angles ($^\circ$) for **1**

| Bond lengths (\AA) | | | |
|-------------------------------|----------|------------|----------|
| Zn1—N1 | 1.989(6) | Zn1—N4 | 1.993(6) |
| Zn1—N2 | 1.997(6) | Zn1—O2 | 2.147(5) |
| Zn1—O1W | 2.421(6) | | |
| Bond angles ($^\circ$) | | | |
| N1—Zn1—N4 | 120.6 | N1—Zn1—N2 | 116.5(3) |
| N4—Zn1—N2 | 120.0(3) | N1—Zn1—O2 | 102.4(2) |
| N4—Zn1—O2 | 94.5(2) | N2—Zn1—O2 | 90.3(2) |
| N1—Zn1—O1W | 84.2(2) | N4—Zn1—O1W | 85.3(2) |
| N2—Zn1—O1W | 83.2(2) | O2—Zn1—O1W | 172.3(2) |

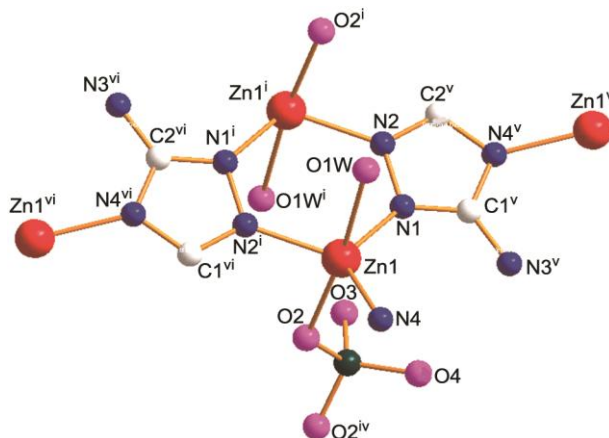


Fig. 1 — View of the coordination environment of the zinc atoms and atz. [Symmetric codes: i: $-x+2, -y, -z+2$; ii: $x-1/2, y, -z+3/2$; iii: $-x+3/2, -y, z-1/2$; iv: $x, -y+1/2, z$; v: $x+1/2, y, -z+3/2$; F: $-x+3/2, -y, z+1/2$. Hydrogen atoms are omitted for clarity].

(by ~ 2.2 Å) than that of the Zn–O bond lengths usually observed in Zn(II) compounds⁶, as also observed in the Zn(II) complex with *o*-aminobenzoic acid and 1,10-phenanthroline (Zn(II)-O4 = 2.560 Å)²⁶. The N–Zn–N angles are 116.5(3), 120.6(2) and 120.0(3)°. The atz ligand has imposed two-fold symmetry and serves as a tridentate bridge in a μ_3 -N¹, N², N⁴ mode, which has been observed in previous studies⁶. The dihedral angles between the triazolyl rings from three different atz ligands are 5.481(214), 22.039(187) and 21.73(12)°, respectively. The complex **1** exhibits a 3D structure containing Zn₂(atz)₂(H₂O)₂SO₄ subunits (Supplementary data, Fig. S2).

The subunit formed by two Zn1 atoms, two coordinated water molecules, one sulfate ion and two triazoles via N¹ and N² atoms of two triazolyl groups has the Zn1–Zn1 distance as 3.4276(13) Å, which is in good agreement with the reported value (3.42 Å)²⁸. The two coordinated water molecules are *cis* to each other. Two atz ligands provide N¹, N² bridging between the zinc centers to form the [Zn₂(tz)₂] (tz = 1, 2, 4-triazole) coordination unit, such Zn₂(tz)₂ coordination unit is rather common in metal triazole chemistry²⁸. Furthermore, the linkage between the [Zn₂(tz)₂] units via Zn atoms and the external N⁴ atoms of the triazoles forms a 2D motif with large quadrilateral cavities parallel to the *ac* plane (Supplementary data, Fig. S3).

Each subunit is twisted at an angle of 49.203(40)° to its neighbouring unit. If the sulfate ions and water molecules are omitted, and both the zinc ions and ligands are regarded as 3-connected nodes and the coordination bonds is taken as linkers, the 2D network can be simplified to be a 4·8² (sql-a) topology¹⁵ (Fig. 2).

The axial sites of the subunits are occupied by sulfate ions, which are tightly coordinated to the zinc with a Zn1–O2 distance of 2.147(5) Å. The sulfate ligands bridge adjacent subunits of the chain through μ_2 -O bridging coordination, leading to infinite chains along the *b* axis (Supplementary data, Fig. S4). Each sulfate ligand exhibits two uncoordinated oxygen atoms, projecting between binuclear building units. Consequently, by coordinating to the external μ_2 -O atoms of sulfate ions, the Zn atoms of the subunits share sulfate ions to form a non-interpenetrating 3D structure with quadrilateral channels of approximate dimensions 6.0334(15) × 5.9643(16) Å (Fig. 3), in which interstitial water molecules are located (Supplementary data, Fig. S5).

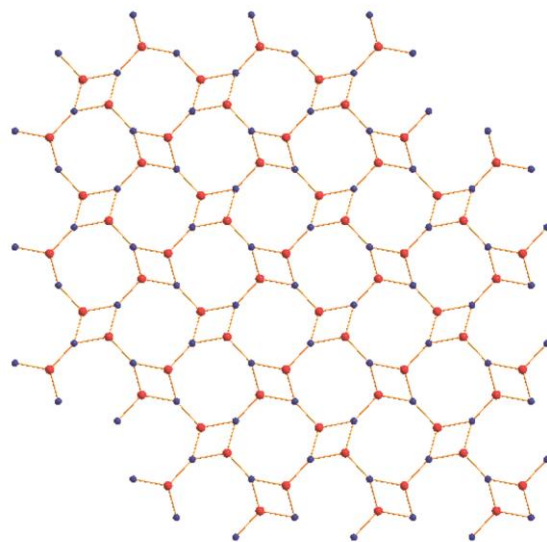


Fig. 2 — Topological representation of the 3-coordinated sql-a topology net in the 2D motif.

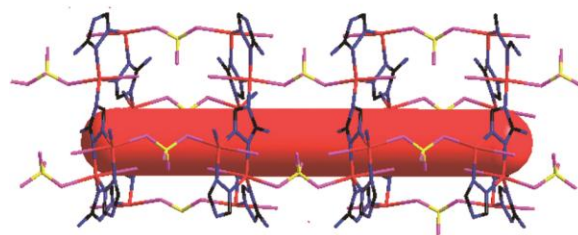


Fig. 3 — 3D structure with quadrilateral channels of approximate dimensions.

The two bridging oxygen atoms of sulfate ions are alternatively oriented in opposite directions towards Zn atoms of the subunits. The solvent-accessible volume of the unit cell is estimated by PLATON program²⁹ to be 407.8 Å³, which accommodates lattice solvent molecules, and is approximately 25.0% of the unit-cell volume (1633.2 Å³). However, most of the spaces are occupied by the substituents, NH₂ and H₂O, leaving substantially no room for gas absorption.

To understand the structure of complex **1** more clearly and easily, the intricate framework was further investigated by topological analysis. As discussed above, each Zn₂(atz)₂(H₂O)₂SO₄ subunit is surrounded by six Zn₂(atz)₂(H₂O)₂SO₄ subunits. Therefore, the subunit can be viewed as a 6-connected node and the μ_2 -sulfate can be regarded as a pillar only to link two metal binuclear units (Supplementary data, Fig. S6). Thus, the whole framework of **1** can be regarded as a 6-connected unimodal pcu topology with the (4¹²·6³) Schläfli symbol¹⁴ (Fig. 4).

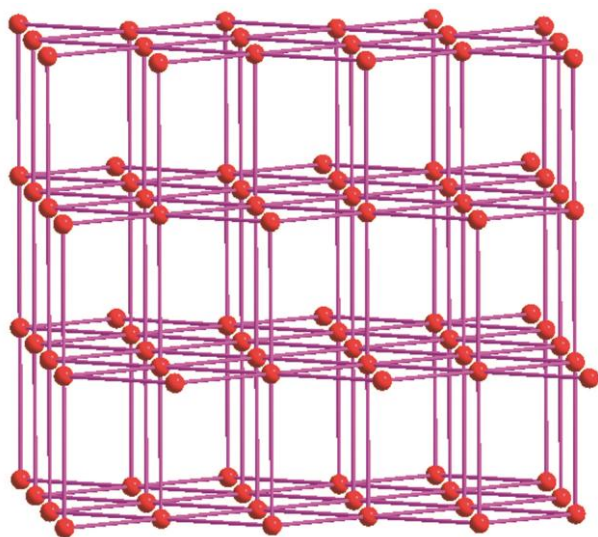


Fig. 4 — Topological representation of the six-coordinated uninodal pcu topology net in complex **1**.

The thermal stability of complex **1** was investigated by thermogravimetric analysis (TGA) (See Supplementary data, Fig. S7, the crystals were dried at room temperature (RT), 100 °C and 120 °C). The TGA curve of **1** shows an initial weight loss of 14.38% from 24.7 to 128.4 °C, corresponding to the removal of four lattice water molecules (calcd. 14.38%), and the framework loses weight from 128.4 to 326.1 °C (obsd. 6.96%, calcd. 7.19%), revealing evacuation of two coordinated water molecules. The largest weight loss was observed with the decomposition of the atz ligand and the rapid collapse of the framework. In addition, after the dehydration at 120 °C, it was observed that the complex decomposed; and the XRD pattern shows very weak diffraction (Supplementary data, Fig. S8).

The solid-state luminescence of free ligand, Hatz and complex **1** were investigated at room temperature. As depicted in Fig. 5, the main emission peak of the free Hatz ligand is at 365 nm ($\lambda_{\text{ex}} = 278$ nm). The emission band may be attributed to ligand-centered $\pi^* \rightarrow \pi$ electronic transitions³⁰. The emission peak is observed at 405 nm ($\lambda_{\text{ex}} = 335$ nm) for complex **1**. Compared with the free Hatz ligand, the emission band of the complex **1** is red shifted (by 40 nm), which may be tentatively attributed to intraligand charge transfer transitions³¹. Compared to the free Hatz ligand, complex **1** exhibits a relatively weak emission peak which may be attributed to the classic photoinduced electron transfer (PET) mechanism³². After the Hatz ligand formed a complex with the metal Zn(II), the excited electron of the ligand was

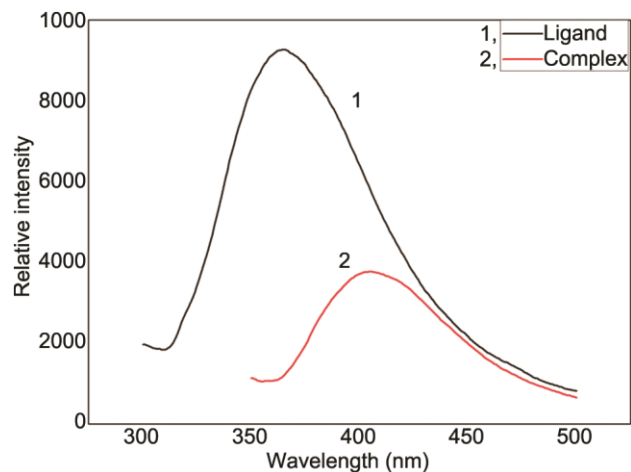


Fig. 5 — Solid-state photoluminescence spectra of free Hatz (1) and complex **1** (2).

then transferred to the LUMO of Zn(II), which induced the fluorescence quenching.

In summary, a metal-organic framework was synthesized at room temperature based on one of the most common SBUs, i.e., the square $\text{Zn}_2(\text{atz})_2(\text{H}_2\text{O})_2\text{SO}_4$ subunit, showing a three-dimensional structure through the sulfate ion bridging ligand. The framework of complex **1** exhibits large square channels containing water molecules, but attempts to remove solvent molecules without damaging the three-dimensional framework were unsuccessful. This work indicates that asymmetric 3-substituted triazole and anionic ligands can be employed as useful linkers for metals with d^{10} configuration, to construct new materials.

Supplementary data

Crystallographic data for the structure of complex **1** have been deposited under the depository number CCDC 433082 with the Cambridge Crystallographic Data Centre, CCDC 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge. (Fax: +49-7247-808-666; Email: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Acknowledgement

The work was supported by the National Natural Science Foundation of China (Grant no. 21161023) and Natural Science Foundation of Yunnan Province, China (Grant no. 2009CD048).

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