

A novel three-dimensional coordination polymer constructed from pyrazine and copper(I): poly[[copper(I)-di- μ_2 -pyrazine- κ^4 N:N'] 3,5-dicarboxy-benzenesulfonate monohydrate]

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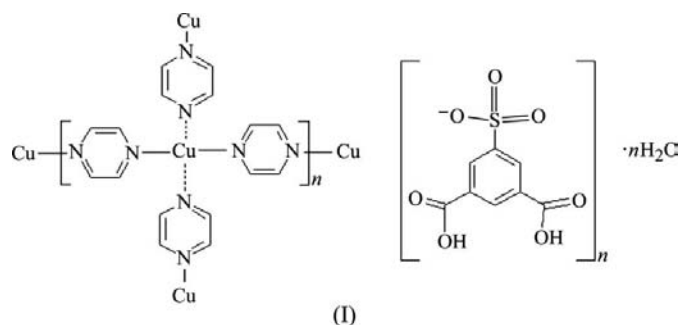
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In the title metal-organic framework complex, $\{[\text{Cu}(\text{C}_4\text{H}_4\text{N}_2)_2](\text{C}_8\text{H}_5\text{O}_7\text{S})\cdot\text{H}_2\text{O}\}_n$ or $\{[\text{Cu}^{\text{I}}(\text{pyz})_2](\text{H}_2\text{SIP})\cdot\text{H}_2\text{O}\}_n$ (pyz is pyrazine and H_3SIP is 5-sulfoisophthalic acid or 3,5-dicarboxy-benzenesulfonic acid), the asymmetric unit is composed of one copper(I) center, one whole pyrazine ligand, two half pyrazine ligands lying about inversion centres, one H_2SIP^- anion and one lattice water molecule, wherein each Cu^{I} atom is in a slightly distorted tetrahedral coordination environment completed by four pyrazine N atoms, with the Cu–N bond lengths in the range 2.017 (3)–2.061 (3) Å. The structure features a three-dimensional diamondoid network with one-dimensional channels occupied by H_2SIP^- anions and lattice water molecules. Interestingly, the guest-water hydrogen-bonded network is also a diamondoid network, which interpenetrates the metal-pyrazine network.

Comment

The design and synthesis of porous coordination polymers is of great interest due to their intriguing topological architecture and significant potential applications in many fields, such as gas molecules, ion exchange, catalytic activity and polymer synthesis (Batten *et al.*, 1998; Abrahams *et al.*, 1999; Fang *et al.*, 2007; Horike *et al.*, 2008; Zhang *et al.*, 2008; Vaqueiro, 2008; Nouar *et al.*, 2008). Although these kinds of materials have promising applications, it would be a big challenge to achieve a major advance without understanding the structural aspects. Thereby, the syntheses of high-dimensional coordination polymers and analyses of the interesting topologies become more important. The classification of structures by Wells (1986) and O'Keeffe (O'Keeffe *et al.*, 2000) laid the foundation for the design and our general understanding of special inorganic compounds, as well as covalent

organic frameworks. On the basis of this classification, a great number of such compounds with interesting topologies are characterized, such as CdSO_4 , NbO , Pt_3O_4 , pyrite, quartz, rutile, halite and sodalite (Luo *et al.*, 2005; Chun *et al.*, 2004). Pyrazine, as a normal rigid linear ligand, has been utilized thus far to synthesize a number of organic-inorganic hybrids (MacGillivray *et al.*, 1994; Kuhlman *et al.*, 1999; Halasyamani *et al.*, 1996; Amo-Ochoa *et al.*, 2007). In order to enrich the coordination chemistry of the three-dimensional open framework constructed from this ligand with one-dimensional channels, in this communication we describe the syntheses and crystal structure of a novel three-dimensional porous coordination polymer constructed from pyrazine (pyz) and Cu^{I} , namely $\{[\text{Cu}^{\text{I}}(\text{pyz})_2](\text{H}_2\text{SIP})\cdot\text{H}_2\text{O}\}_n$ (H_3SIP is 5-sulfoisophthalic acid), (I).



As shown in Fig. 1, the asymmetric unit of (I) consists of one Cu^{I} ion, one whole and two half pyrazine ligands lying about inversion centres, one H_2SIP^- anion and one lattice water molecule. The Cu^{I} centre is coordinated by four N atoms from pyrazine ligands to form a slightly distorted tetrahedral configuration, in which the four Cu–N bond lengths are 2.017 (3), 2.033 (3), 2.054 (3) and 2.061 (3) Å, and the N–Cu–N bond angles are in the range 98.21 (11)–123.27 (11)° (Table 1). The mean Cu–N bond length of 2.042 Å is similar to that found in $[\text{Cu}(2,5\text{-Me}_2\text{-pyz})_2]\text{PF}_6$ (2,5-Me₂-pyz is 2,5-dimethylpyrazine; Otieno *et al.*, 1993).

The linear pyrazine ligands act as pillars along different directions and link Cu^{I} ions to form an extended three-

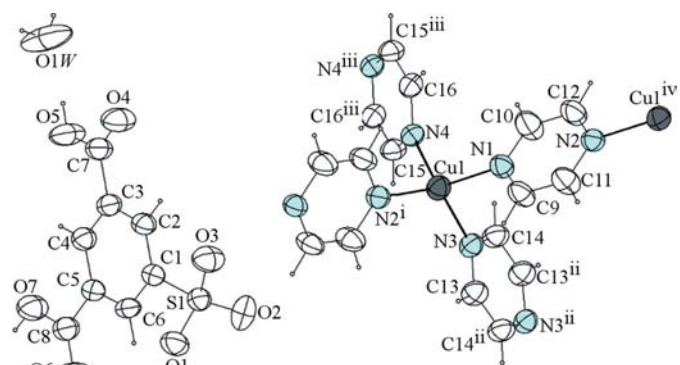


Figure 1
A view of the structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level. [Symmetry codes: (i) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + 2, -y, -z$; (iii) $-x + 1, -y, -z$; (iv) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

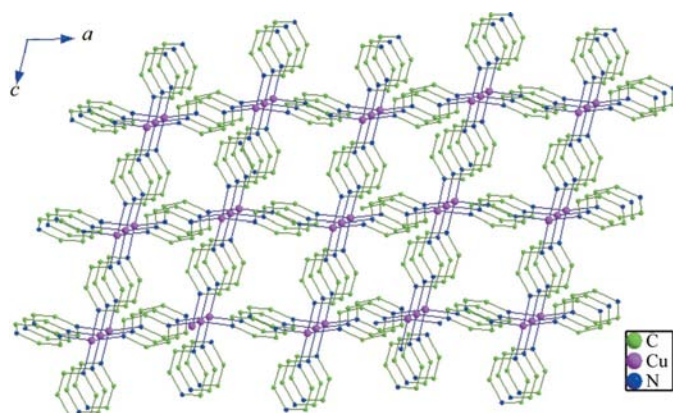


Figure 2
A view of the three-dimensional network of (I) along the *b* axis.

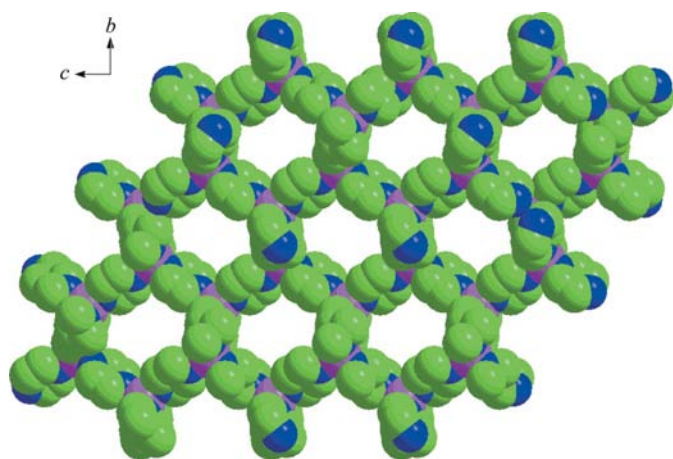


Figure 3
A space-filling view of the three-dimensional framework of (I).

dimensional porous coordination network (Fig. 2). As a consequence of this assembly, one-dimensional channels occupied by guest water molecules and H_2SIP^- anions are formed. As shown in Fig. 3, the one-dimensional porous channels in the three-dimensional open framework features a large hexagonal 26-membered ring with approximate dimensions $15.1 \times 13.0 \text{ \AA}$, which contains six Cu atoms and six pyrazine ligands. Although a good number of hexagonal-shaped metallacycles are known in coordination polymers, such nano-sized metallacycles constructed from Cu^{I} and simple linear ligands gusted by H_2SIP^- anions and water molecules are still unprecedented.

A better insight into the nature of this intricate framework can be achieved by the application of a topological approach, *i.e.* reducing multidimensional structures to simple node and connection nets. As depicted in Fig. 4, each Cu^{I} site in (I) is coordinated by four pyrazine N atoms, while each pyrazine ligand serves as a two-connected node bridging two Cu^{I} atoms. Therefore, the Cu^{I} ion can be simplified to a four-connected node and, accordingly, each pyrazine ligand becomes a two-connected linker and the overall topology can thus be described as a diamondoid network.

Notably, the free water molecules and the H_2SIP^- anions are encapsulated in the channels and are further linked with

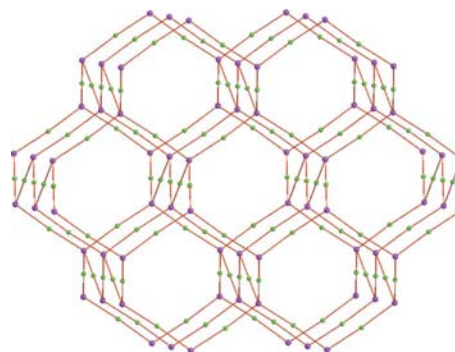


Figure 4
A topological view of the (2,4)-connected network for (I). Dark and light (purple and green in the electronic version of the paper) balls denote the Cu^{I} ions and pyrazine ligands, respectively.

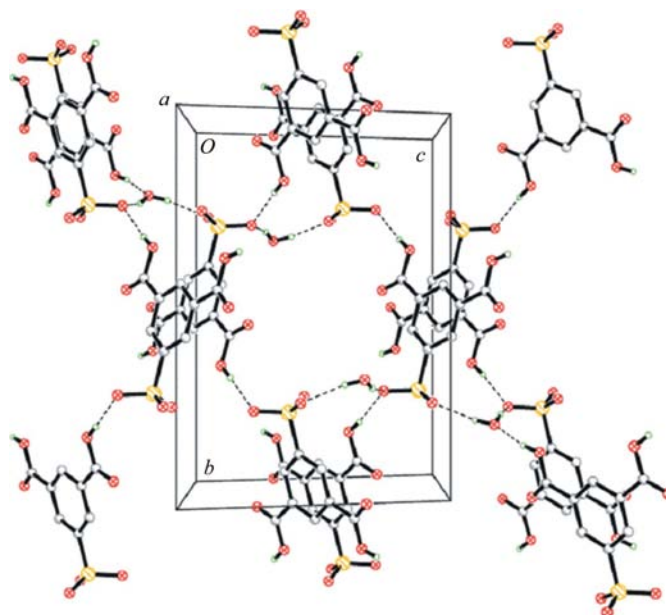


Figure 5
A view of the hydrogen-bonded stacking along the *a* axis in the guest-water molecules for (I).

each other through $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions into a three-dimensional supramolecular open framework, as shown in Fig. 5. There are three types of hydrogen bonds: (*a*) between the lattice water molecules and sulfonate O atoms [$\text{O1W} \cdots \text{O3} = 2.790 (5) \text{ \AA}$ and $\text{O1W} \cdots \text{O1} = 2.903 (4) \text{ \AA}$]; (*b*) between a carboxyl O atom and a lattice water molecule [$\text{O5} \cdots \text{O1W} = 2.578 (5) \text{ \AA}$]; (*c*) between a carboxyl O atom and a sulfonate O atom [$\text{O7} \cdots \text{O1} = 2.767 (4) \text{ \AA}$]. Thus, the guest molecules have a significant influence on the coordination geometry of the host metal ions. The guest-water hydrogen-bond network is also a diamondoid network, which interpenetrates the metal-pyrazine network.

Complex (I) is stable in air and insoluble in water and most organic solvents, so no additional measurements in solution could be performed. Interestingly, (I) shows strong photoluminescence in the solid state, with an emission maximum at 645 nm upon excitation at 385 nm at room temperature. According to the structural features of the compound, the emission band might be assigned to a combination of metal-to-

ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT). The compound appears to be a good candidate as a novel hybrid inorganic–organic photoactive material.

In summary, a new three-dimensional porous metal–organic framework with open channels featuring an unusual (2,4)-connected topology has been synthesized and characterized. The structure of (I) provides another valuable prototype of (2,4)-connected nets which may be important for the design of porous coordination polymers (PCPs).

Experimental

A mixture of Cu(OH)₂ (19.5 mg, 0.2 mmol), NaH₂SIP (26.8 mg, 0.1 mmol), pyrazine (12.1 mg, 0.15 mmol) and water (15 ml) was heated at 448 K for 5 d. Black block-shaped crystals of (I) were obtained when the sample was cooled to room temperature at a rate of 5 K h⁻¹. The crystals were recovered by filtration, washed with distilled water and dried in air (yield 42.3% based on Cu). Analysis calculated for C₁₆H₁₅CuN₄O₈S: C 39.43, H 3.08, N 11.50%; found: C 40.02, H 3.56, N 11.71%. IR spectrum (KBr pellet, cm⁻¹): 3440 (*ms*), 1713 (*s*), 1478 (*s*), 1417 (*s*), 1241 (*w*), 1187 (*ms*), 1157 (*m*), 1101 (*m*), 1037 (*s*), 1000 (*ms*), 847 (*w*), 800 (*s*), 755 (*ms*), 721 (*ms*), 680 (*w*), 669 (*ms*), 653 (*w*), 622 (*s*), 574 (*w*), 485 (*ms*), 466 (*w*), 449 (*ms*).

Crystal data

[Cu(C ₄ H ₄ N ₂) ₂](C ₈ H ₅ O ₇ S)·H ₂ O	<i>V</i> = 1899.7 (6) Å ³
<i>M_r</i> = 486.94	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ /c	Mo <i>K</i> α radiation
<i>a</i> = 11.124 (2) Å	<i>μ</i> = 1.31 mm ⁻¹
<i>b</i> = 15.709 (3) Å	<i>T</i> = 293 (2) K
<i>c</i> = 11.337 (2) Å	0.33 × 0.24 × 0.16 mm
<i>β</i> = 106.48 (3)°	

Data collection

Siemens SMART CCD area-detector diffractometer	17404 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4323 independent reflections
<i>T</i> _{min} = 0.692, <i>T</i> _{max} = 0.810	2960 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.059

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.049	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> (<i>F</i> ²) = 0.111	<i>Δρ</i> _{max} = 0.36 e Å ⁻³
<i>S</i> = 1.01	<i>Δρ</i> _{min} = -0.30 e Å ⁻³
4323 reflections	
277 parameters	
5 restraints	

H atoms attached to C atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The carboxyl H atoms were located in a difference Fourier map and were refined with O–H distance restraints of 0.86 (2) Å. Water H atoms were located in a difference map and refined with O–H and H···H distance restraints of 0.85 (2) and 1.39 (1) Å, respectively, and with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: SMART (Siemens, 1994); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Table 1
Selected geometric parameters (Å, °).

Cu1–N2 ⁱ	2.017 (3)	Cu1–N1	2.054 (3)
Cu1–N3	2.033 (3)	Cu1–N4	2.061 (3)
N2 ⁱ –Cu1–N3	123.27 (11)	N2 ⁱ –Cu1–N4	103.33 (11)
N2 ⁱ –Cu1–N1	110.21 (11)	N3–Cu1–N4	107.02 (11)
N3–Cu1–N1	98.14 (11)	N1–Cu1–N4	115.53 (11)

Symmetry code: (i) *x*, $-y + \frac{1}{2}$, *z* + $\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1W–H1WA···O3 ^v	0.830 (19)	1.96 (2)	2.790 (4)	178 (6)
O1W–H1WB···O1 ^{vi}	0.829 (19)	2.11 (3)	2.903 (4)	159 (6)
O5–H5···O1W	0.82	1.76	2.578 (4)	171
O7–H7···O1 ^{vii}	0.82	1.97	2.766 (4)	165

Symmetry codes: (v) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x, -y, -z + 1$; (vii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3085). Services for accessing these data are described at the back of the journal.

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