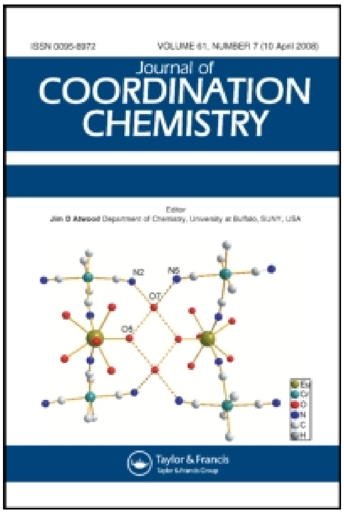

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Hydrothermal synthesis and crystal structure of a metal–organic compound with unique pseudo-hexagonal water channels: $[Cu^{II}(phen)(sal)]\cdot 0.5H_2O$ (phen = 1,10-phenanthroline, sal = salicylic acid)

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This article presents a metal–organic compound $[Cu^{II}(phen)(sal)]\cdot 0.5H_2O$ (**1**) with intriguing structural motif of 3D hexagonal water channels. Furthermore, IR, element analysis, and TGA were employed to characterize it. The TG-DTA showed that this structure is stable to 300°C. Compound **1** belongs to the hexagonal system, space group *R*-3, $a = 33.337(5)$ Å, $b = 33.337(5)$ Å, $c = 9.4599(19)$ Å, $\gamma = 120°$, $V = 9105(3)$ Å^3, $Z = 18$.

Keywords: 1,10-Phenanthroline; Salicylic acid; Water channel; Porous materials

1. Introduction

The versatility of metal–organic chemistry offers opportunities to construct multifunctional materials based on the assembly of molecular building blocks. Such an approach can lead to the design of coordination polymers with intriguing architectures and potential applications [1–3]. Inorganic–organic open-framework materials has become one of intense research activity [4–9]. While one of the objectives of the research into open-framework solids is to find materials possessing channels and other features that make them porous, which can impart potential catalytic and sorption properties, the discovery of fascinating architectures of different dimensionalities has been equally exciting. The metal carboxylates are particularly interesting in that they not only form open-framework structures resulting from the presence of the carboxylate function itself, but also where the carboxylate group acts as a linker between metal–organic moieties [10]. Herein, we report one copper complex with phen and dideprotonated (sal^{2-}) salicylate ligands, namely $[Cu^{II}(phen)(sal)]\cdot 0.5H_2O$ (**1**), which has a unique pseudo-hexagonal water channel formed by six centrosymmetric dimeric units $[Cu^{II}_2(phen)_2(sal)_2]$ *connected by* π–π stacking.

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2. Experimental

2.1. *Materials and physical measurements*

All reagents were bought from commercial sources and used without further purification. An infrared spectrum was obtained from KBr pellets on a Nicolet Magna-IR 560 spectrophotometer in the 400–4000 cm^{-1} region. The elemental analysis was carried out on a Perkin-Elmer 2400 analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV spectrometer.

2.2. *Synthesis*

$[Cu^{II}(phen)(sal)] \cdot 0.5H_2O$ (**1**), was synthesized under hydrothermal conditions. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.30 g), 1,10-phenanthroline (0.08 g), salicylic acid (0.07 g) and water (10 mL) in the molar ratio of 5 : 2 : 2 : 667 was reacted at 180°C for 60 h in a 25 mL Teflon-lined stainless-steel vessel. After the reaction vessel cooled to room temperature at a rate of ca 5°C h^{-1}, dark blue block single crystals of **1** in 55% yields (based on copper) were obtained. Anal Calcd for $C_{19}H_{12}CuN_2O_{3.5}$ (%): C, 71.05; H, 3.67; N, 8.65. Found: C, 70.36; H, 3.73; N, 8.64.

2.3. *X-ray crystal structure determination*

Single-crystal X-ray diffraction of complex **1** was performed on a Bruker SMART 1000 CCD diffractometer equipped with graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω–2θ scan mode in the range of $3.23 < \theta < 24.99°$ for **1** at 293(2) K. All data were corrected for absorption by a semi-empirical method using SADABS program. The program SAINT [11] was used for integration of the diffraction profiles.

The structures were solved by direct methods using the SHELXS program of the SHELXL-97 package and refined with SHELXL [12]. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. The hydrogen atoms of the ligands were placed in geometrically calculated positions. Further crystallographic data and experimental details for structure analysis of complex **1** is summarized in table 1, and the selected bond lengths and angles with estimated standard deviations are in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single crystal X-ray diffraction analysis reveals the title complex **1** is constructed from a square planar $[Cu^{II}(phen)(sal)]$ moiety and half lattice water (figure 1), and each pair of the square planar moieties are aligned as a centrosymmetric dimeric unit. The coordination geometry of Cu(II) ions (bond valence calculations give values of 1.92 for Cu atom [13]) in the moieties is five-coordinate, square pyramidal by two nitrogen

Table 1. Crystal data and details of structural determination of compound **1**.

Formula	$C_{19}H_{12}CuN_2O_{3.5}$
Fw	387.85
Space group	Hexagonal (R-3)
a (Å)	33.337(5)
b (Å)	33.337(5)
c (Å)	9.4599(19)
γ (°)	120
V (Å^3)	9105(3)
D (Mg cm^{-3})	1.273
T (K)	293 ± 2
R_1 and wR_2 [$I > 2\sigma(I)$]	0.0676, 0.1711
Goodness-of-fit (GOF)	1.054

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu1–N1	2.012(5)	Cu1–N2	2.013(5)	Cu1–O1	1.879(4)
Cu1–O3	1.886(4)	C19–O1	1.260(8)	C19–O2	1.246(8)
O(3)–C(13)	1.336(6)	O(1)–Cu(1)–N(1)	90.3(2)	O(3)–Cu(1)–N(1)	174.1(2)
O(1)–Cu(1)–O(3)	95.37(18)	O(3)–Cu(1)–N(2)	92.41(19)	N(1)–Cu(1)–N(2)	81.8(2)
O(1)–Cu(1)–N(2)	168.2(2)	C(12)–N(1)–Cu(1)	114.3(4)	C(19)–O(1)–Cu(1)	129.3(4)
C(1)–N(1)–Cu(1)	128.8(5)	O(2)–C(19)–O(1)	120.5(7)	O(2)–C(19)–C(18)	117.9(6)
O(1)–C(19)–C(18)	121.6(6)	C(13)–O(3)–Cu(1)	123.8(4)		

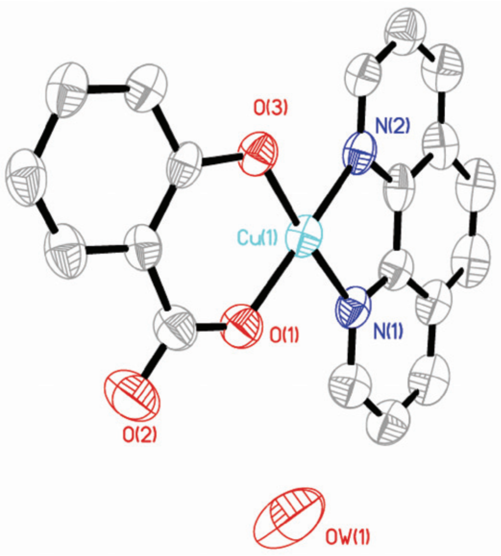

Figure 1. ORTEP view of the building block units in crystalline **1**. Only parts of atoms are labeled, and all H atoms are omitted for clarity.

atoms from a phen ligand (bond distances of Cu–N fall in the range of 2.012(5)–2.013(5) Å), two oxygen atoms of the dideprotonated sal^{2-} ligand (distances of Cu–O vary from 1.879(4) to 1.886(4) Å), and an oxygen atom of a deprotonated hydroxyl group of the sal^{2-} ligand from another square planar [Cu^{II}(phen)(sal)] moiety occupies the apical position with Cu–O of 2.570 Å, longer than the two Cu–O(sal^{2-}) bonds. The coordination environment of Cu(II) is similar to the reported compound in main configuration [14–16]. The Cu–Cu distance and Cu–O–Cu angle for this centrosymmetric dimeric unit with the double bridging oxygen μ_2-O3, is 3.310 Å and 94.68°.

As shown in figures 2 and 3, the unique pseudo-hexagonal water channels build from six centrosymmetric dimeric units $[\mathrm{Cu}_2^{\mathrm{II}}(\mathrm{phen})_2(\mathrm{sal})_2]$ (every three centrosymmetric dimeric units show a D_{3h} symmetry in clockwise or counterclockwise arrangement, respectively) as the Secondary Building Units (SUBs) *via* π–π stacking effect (containing two modes: the interaction along the *c* axis with the interlayer distance 3.7 Å for phen–phen; another interaction along the *ab* plane with the point–plane distance 3.6 Å for sal^{2-}–sal^{2-}). Every hexagonal channel encapsulates six free water molecules hydrogen bonded to the sal^{2-} ligand (Ow1–O2: 3.082 Å and Ow1–O1: 3.155 Å), in a six-membered puckered arrangement of O atoms with the edge distance of 6.896 Å (O2a, O2b, O2c, O2d composed the quadrangular plane, while O1a, O1b displaced the plane with the opposite fashion) (figure 4). Furthermore, we evaluated the potential capability of the hexagonal water channels by PLATON [17], which showed that the total void space in the hexagonal water channels corresponds to 2050.4 Å^3, 22.5% of the cell volume. If the free water molecules in the channels are omitted, the void space will extend to 2605.7 Å^3, 28.6% of the cell volume.

Compared with the similar coordination polymer $\{[\mathrm{Cu}_2^{\mathrm{II}}(\mathrm{phen})_2(\mathrm{sal})_2]\cdot 2\mathrm{H_2O}\}$ [16], the coordination sphere and basal conformation for Cu(II) can be viewed as the same, but the packing mode and synthesis method is different: the reported compound was obtained from the neutral organic solvent DMF-DMSO and belonged to monoclinic with space group $P2_1/n$, whereas compound **1** is synthesized by hydrothermal reaction

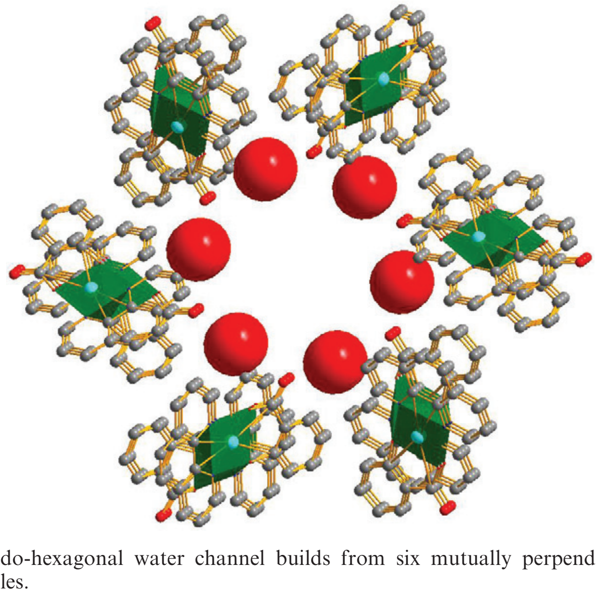

Figure 2. The pseudo-hexagonal water channel builds from six mutually perpendicular SUBs with six capped water molecules.

and belongs to hexagonal space group *R*-3, resulting in the unique structural motif of 3D hexagonal water channel.

3.2. *Spectral characterization and thermal properties of 1*

The absorption bands (1598, 1575, 1518, 1136, 844, 720, 430 cm^{-1}) are assigned to phen ligand. Features at 1541, 1429 cm^{-1} are ascribed to the asymmetric and symmetric stretching vibrations of carboxylate group. The absorption at 3647 cm^{-1} is attributed to the stretching vibration of hydroxyl.

Thermogravimetric analysis of **1** was carried out in the temperature range 30–600°C (heating rate = 5°C min^{-1}) (figure 5). TG-DTA curve reveals that this material initially loses surface water at 115°C but remains stable to further loss of water up to 300°C,

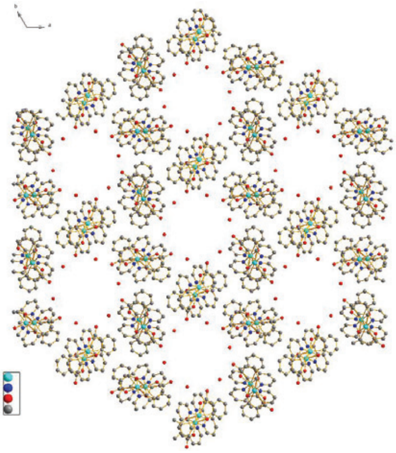

Figure 3. The 3D hexagonal channel as water container.

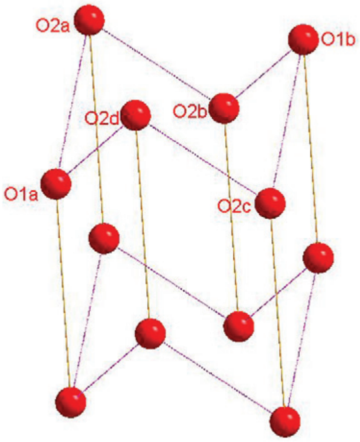

Figure 4. The six capped water molecules show a hexamethylene-type conformation.

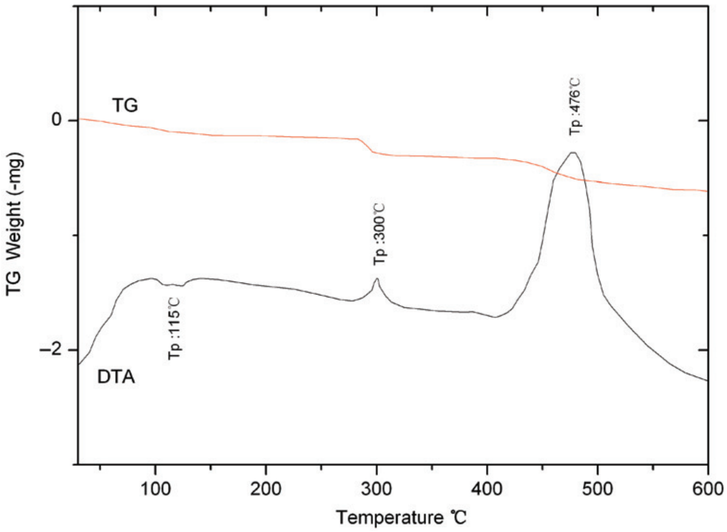

Figure 5. The TG-DTA of **1**.

the last two weight losses between 300–600°C suggest the decomposition of compound **1**, which means the 3D water channels can be stable to 300°C.

4. Conclusion

In summary, we have synthesized a 3D hexagonal water container via hydrothermal synthesis. Considering the 3D hexagonal channels, the crystal may be applied as potential storage material such as molecular storage, ion exchanging and so on.

Supplementary material

Crystallographic data for the structure reported in this article has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (No: 288543). Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336-033; Email: deposit@ccdc.cam.ac.uk).

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