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Microwave assisted hydrothermal synthesis of a novel Cu^I-sulfate-pyrazine MOF

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Abstract

A new 3D coordination copper polymer has been synthesised under microwave heating hydrothermal conditions. Microwave irradiation reduces the time of reaction considerably, suggesting the effectiveness of this methodology in the synthesis of metal-organic frameworks. It is noteworthy that microwave assisted synthesis produces monocrystals suitable for X-ray diffraction studies, reducing reaction time and with higher yield than the classical hydrothermal procedures. The compound presented here, $[Cu_2(pyz)_2(SO_4)(H_2O)_2]_n$ (pyz = pyrazine), has been crystallographically characterised to be a threefold interpenetrated three-dimensional coordination (10,3)-b network.

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Open-framework metal–organic polymers, derived from the combination of selected transition metal and multidentate bridging ligands, have attracted much attention in the last decades due to their potential as purpose-built materials with practical properties such as gas storage [1–4], catalysis [5], optics [6] and magnetisms [7]. In addition, they have been recently investigated as novel nanomaterials [8–12]. These assemblies of metal complexes are predominantly prepared by slow diffusion techniques or by hydro(solvo)thermal reaction methods [13–16], in processes that can take up to several weeks.

A faster route to metal–organic frameworks (MOFs) synthesis is still a challenging task for solid-state materials if they are to be produced in a much larger scale. Micro-wave dielectric heating, with the possible advantage of

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enhanced product yields and reduced reaction times, emerges as a feasible approach and begins to be entrenched not only in synthetic organic chemistry [17,18] but also in zeolites-type inorganic hybrid materials [19], and for nano-scale particle preparations [20]. However, the employment of this technique for the construction of well-defined MOFs accounts with very scarce reported structures [21–23]. Just recently, microwave methodology has been successfully applied with promising results as an alternative in the synthesis of coordination polymers which generally needs several days for their hydrothermal crystallization.

Herein we communicate that the reaction between $CuSO_4$ and pyrazine in water under hydrothermal conditions could be reproduced using microwave radiation, yielding in both cases the air-stable coordination polymer $[Cu_2(pyz)_2(SO_4)(H_2O)_2]_n$, **1**. This compound has an intricate structure consisting of three independent 3D infinite

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networks in which the voids related with one framework are occupied by the other two, which are, at the same time, inextricably entangled, rendering a threefold interpenetrated net [24]. Microwave reaction was contrasted with the same reaction carried out under conventional hydrothermal synthesis. Additionally, we have investigated the TGA profile and reaction time effects on the microwave synthesis of 1. The conventional hydrothermal reaction between CuSO₄ and pyrazine in a 1:1 molar ratio (in the presence of benzoic acid, pH 3.2), at 180 °C for 24 h, produced red acicular crystals of $[Cu_2(pyz)_2(SO_4)(H_2O)_2]_n$ (1) in a 46.2% yield [25]. The coloration suggested the reduction of the Cu(II) metal centres to Cu(I) as corroborated by X-ray diffraction analyses. At high temperatures, nitrogen-rich organic ligands are well known to serve as effective reducing agents for such process [14].

Remarkably, microwave irradiation mimicked the reducing power conditions necessary to form 1 [25]. However, while hydrothermal synthetic procedures rendered compound 1 as the only phase-pure product, the stoichiometrical reaction carried out under microwave methods after 1 h, produced blue crystals of the 1D coordination polymer [Cu(pyz)(SO₄)(H₂O)]_n [26]. When reaction time was set to 3 h, red crystals of 1 were isolated, with a low yield (8.7%). Reaction carried out for 6 h, increased the yield of 1 up to 37.7% (the 6 h hydrothermal reaction gave 1 in a 12.0% yield). Hence, microwave techniques have proved to effectively abridge reaction time with a remarkable higher yield performance (12.0 vs 37.7%).

The thermal degradation (Fig. 1) profile of **1** under synthetic air, evidences the concomitant mass loss of the coordinated water molecules along with half of the pyrazine ligand content (exp. 72.6%, calc. 72.3%), in a process that begins at 100 °C. The residue is stable from 260 to 270 °C and decomposes further, between 270 and 420 °C, losing the remaining pyrazine molecules (exp. 53.8%, calc. 53.2%). Then finally undergoes the last decomposition at 580 °C yielding Cu₂S above 730 °C (exp. 37.9%, calc. 38.4%).

X-ray quality monocrystals of the compound were obtained both by classical and microwave assisted hydrothermal procedures. The unit cell parameters of the sample obtained by microwave radiation [27] are well consistent with those observed for that synthesised for one day at 180 °C under hydrothermal conditions. A view of the coordination sphere of the copper atom is depicted in Fig. 2. The Cu(I) centre is coordinated to four ligands: two pyrazine, a sulfate and a water molecule; while pyrazine and SO_4^{2-} act as bridges, the water molecule is coordinated only to one copper atom and forms two short hydrogen bonds: $O1w(H2w) \cdots O1^{i}$ (2.757(2) Å), and $O1w(H1w) \cdots O2^{ii}$ (2.760(2) Å) (ⁱ -x + 3/2, -y + 1/2, -z; ⁱⁱ x - 1/2, y + 1/2, z) with two adjacent SO₄²⁻ belonging to the other two independent networks. The coordination geometry of the copper atom is tetrahedral, with an appreciable distortion. Angles around Cu range from 102.07(6) (N1-Cu-O1) to 125.27(7) (N11–Cu–N1), Cu coordination bond distances range from 1.9550(16) (Cu-N11) to 2.1762(15) Å (Cu-O1w). Dihedral angle between both pyrazines is 64.53°. Cu coordinates to the sulfate ligand through an oxygen atom (O1), its symmetry related O1' coordinates to a neighbour Cu', the remaining oxygen atoms O2 and O2' are uncoordinated.

After growth of this single structure, a 3D polymeric net is generated. This single net is assembled by fused rings containing ten metals (see Fig. 3), which are shared by adjacent rings. The ring hollows are interpenetrated by other two different rings (see Fig. 4) coming from other two independent nets symmetrically generated. Thus, the crystal structure of **1** can be defined is a (10,3)-b [24] threefold interpenetration of three independent single nets as described above (see Fig. 5).

In summary, in this communication we present the results of a hastened crystallization process of a novel 3D Cu(I) coordination polymer by using microwave irradiation. The results were compared with those obtained under conventional hydrothermal conditions which require longer reaction times. We believe that these results are



Fig. 1. Thermogravimetric curve of compound 1 from room temperature to 800 °C.



Fig. 2. View of the coordination sphere of Cu with atom numbering scheme. Selected bond distances (Å) and angles (°) for compound 1: Cu-N1 1.9874(17), Cu-N11 1.9550(16), Cu-O1 2.1092(14), Cu-O1w 2.1762(15), N1-C1 1.348(3), S1-O1 1.4852(15), S1-O2 1.4688(13), N11-Cu-N1 125.27(7), N11-Cu-O1 118.64(6), N1-Cu-O1 102.07(6), N11-Cu-O1w 105.12(7), N1-Cu-O1w 109.25(6), O1-Cu-O1w 91.06(6).



Fig. 3. View of a closed $Cu_{10}(pyz)_6(SO_4)_4$ ring. Water and shared-pyrazine ligands were omitted for clarity.



Fig. 4. Schematic representation of a single ring (up), with interpenetration model (down). Cu atoms placed in the rectangle vertexes are coplanar.



Fig. 5. Schematic representation of the three interpenetrating networks of 1, with the Cu atoms sitting at the nodes (a) and view of an isolated network (b).

valuable for the future preparations of MOFs in commercial scale.

Supplementary material

CCDC 636375 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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- [25] Syntesis of 1: The precursors mixture, $CuSO_4$ (0.500 g, 3.132 mmol), pyrazine (0.251 g, 3.132 mmol), benzoic acid (0.381 g, 3.132 mmol) and 15 mL of H₂O, were loaded in a microwave-specified 70 mL TFM autoclave, sealed and placed in a microwave reactor. The reaction mixture was heated to the reaction temperature of 180 °C in 20 min and maintained for a maximum of 6 h. The vessel was then cool down to room temperature in 2 h. The resulting red crystals were filtered on a glass frit, washed with warm water and dried under air. (0.248 g, yield: 37.6%, based on Cu.) Alternatively, the same amount of

reactant mixture heated in a 23 mL Teflon-lined autoclave and heated at 180 °C for one day gave crystals of the same product (0.310 g, 46.2% yield, based on Cu). Anal. Calc. for $C_8H_{12}N_4O_6SCu_2$: C, 22.91%, H, 2.88%, N, 13.36%, S 7.65%. Found: C, 22.82%, H, 2. 87%; N, 13.27%, S 7.60%.

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- [27] Crystal data of the sample prepared under microwave conditions were measured as follows: $C_8H_{12}Cu_2N_4O_6S$, $Mr = 419.36 \text{ g mol}^{-1}$, red prisms $(0.10 \times 0.08 \times 0.08 \text{ mm})$, Monoclinic, C2/c, a = 10.9841(3) Å, b = 11.7707(3) Å, c = 11.3163(2) Å, $\beta = 114.3500(10)^\circ$, V = 1332.94(6) Å³, Z = 4, T = 100(2) K, $D_{calcd} = 2.090 \text{ g cm}^{-3}$, F(000) = 840, $R_1 = 0.0245$, $wR_2 = 0.0660$, $S(F_0 > 2\sigma(F_0)) = 1.053$.