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Water-based synthesis and characterisation of a new Zr-MOF with a unique inorganic building unit†

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A new, microporous Zr-MOF was obtained using 2,5-pyrazinedicarboxylic acid (H₂PzDC). The linker leads to the formation of a new 1D inorganic building unit composed of μ-OH bridged {Zr₆O₄(OH₄)} clusters which are arranged in a hexagonal array and connected by the PzDC²⁻ ions. The structure was determined from powder X-ray diffraction data.

Metal organic frameworks (MOFs) have been intensively investigated for various applications like gas storage,¹ gas separation,² catalysis,³ heat transformation⁴ or drug delivery⁵ due to their high specific surface areas and the diversity of their structures.⁶ In particular Zr-MOFs are studied for possible applications, due to their thermal and chemical stability.⁷,⁸ An outstanding structural feature in carboxylate-based Zr-MOFs is the presence of hexanuclear clusters of composition {Zr₆O₄(OH₄)} which are also well known from molecular Zr⁴⁺ complexes (Fig. 1, bottom, left).⁹ The clusters are readily formed under various reaction conditions and dominate the structural chemistry of Zr-MOFs. The first example that contains this inorganic building unit (IBU) is UiO-66 ([Zr₆O₄(OH₄)(BDC)₆], BDC²⁻ = benzenedicarboxylate, UiO = University of Oslo), which was reported in 2008. In the ideal structure the IBUs are twelvefold connected and form a fcu network topology.¹⁰ Isoreticular structures have been reported as well with linkers of different sizes, e.g., DUT-52 (DUT = Dresden University of Technology)¹¹ or UiO-67,¹² Zr-Fum,¹² ZrSQU¹³ or for example with functionalized terephthalic acids.¹⁴,¹⁵ Other topologies have been observed as well, when the hexanuclear IBU is ten (DUT-69¹⁶), eight (DUT-67,¹⁶ DUT-51,¹⁷ MOF-81,¹⁸ MOF-545¹⁹ or PCN-521, PCN = porous coordination network²⁰) or six connected (MOF-808¹⁰). Exceptions where other IBUs are observed are found in the structures of MIL-140 (MIL = Material Institute Lavoisier)²¹ and PCN-221²² where {Zr[μ₃-O]₃O₄} chains (Fig. 1, top, right) and {ZrO₆} clusters (Fig. 1, middle, left) are incorporated. The {ZrO₆} cluster has been reported once and the structure refinement lead only to rather high R₁/wR₂ values (0.1924/0.4359 for Zr-PCN-221(Cu)). In the phosphonate- and phenolate-based MOFs UPG-12³ (UPG = University of Perugia) and MIL-163,²⁴ ZrO₆-polyhedra (Fig. 1, top, left) and edge-sharing ZrO₆-polyhedra IBUs (Fig. 1, middle, right) have been observed, respectively (Table S1.³, ESI†).

Zr-MOFs have been mainly synthesized under autogenous pressure using DMF as the solvent,⁴,¹⁰,¹⁶,¹⁸ however, recently green synthesis routes and reaction upscaling have been reported.²⁵–³⁰ For green syntheses the choice of the metal source and the solvent employed are crucial, and reactions in water, ethanol, acetic or formic acids are usually preferred.

Herein we report the water-based synthesis and detailed characterization of a new Zr-MOF, denoted as CAU-22 (CAU = Christian-Albrechts-Universität) which contains 2,5-pyrazinedicarboxylate ions (PzDC²⁻) and a unique 1D IBU of edge-sharing hexanuclear {Zr₆O₄(OH₄)} clusters.

The linker H₂PzDC was synthesized as previously reported³¹ (see S2, ESI†) and to the best of our knowledge it has only been
The discovery and synthesis optimization of the title compound was carried out in 2 ml Teflon reactors using high-throughput methods as established in our group, and setting the reaction time and temperature to 24 h and 120 °C. Initially the influence of the Zr salt on the product formation was evaluated. Using Zr(SO4)2·4H2O and ZrO(NO3)2·xH2O in a solvent mixture of water and formic acid yielded exclusively X-ray amorphous products, while the use of ZrCl4 and ZrOCl2·8H2O resulted in crystalline products. Systematic optimization of the solvent composition (formic acid to H2O ratio) led to a highly crystalline product (Fig. 2). Synthesis details and PXRD patterns are given in the supporting information (Table S3.1 and Fig. S3.1–S3.3, ESI†).

For both metal sources, ZrCl4 and ZrOCl2·8H2O, an equimolar metal to linker ratio and similar formic acid : H2O ratio of 70 : 30 and 50 : 50, respectively, results in the formation of the most crystalline reaction product. For full characterization of CAU-22, the synthesis was scaled up in a 30 ml Teflon reactor keeping the optimized reaction conditions constant and using ZrOCl2·8H2O as the metal source, which is much cheaper compared to ZrCl4.

CAU-22 was only obtained as a microcrystalline product and hence the structure had to be determined from PXRD data. Indexing was carried out with Topas35 and the structure was solved by direct methods using the program suit Expo. Each resulting 1D IBUs is composed of hexanuclear clusters \([\text{Zr}_6\text{O}_4\text{(OH)}_4]^{3-}\) linked by edge-sharing of hexanuclear clusters \([\text{Zr}_6\text{O}_4\text{(OH)}_4]\) via \(\mu\)-OH groups along the c-axis, bridging \(\mu\)-OH groups shown in green, O atoms of formate groups in blue, while the rest of the O atoms \((\mu_1\text{-O}, \mu_2\text{-OH}, \text{H}_2\text{O}, \text{OH}^-, \text{CO}_2^-\text{ groups})\) are shown in red. Bottom left: proposed hydrogen bonding (red dotted line) between the bridging \(\text{PzDC}^{2-}\) ions and \(\text{H}_2\text{O}/\text{OH}^-\) molecules coordinating to the \(\text{Zr}^{4+}\) ions (view along [010]); bottom right: connection of the 1D IBUs by the \(\text{PzDC}^{2-}\) ions (view along [001]) which leads to the formation of 1D pores with a diameter of ca. 3 Å.

The latter has been proposed for many other Zr-MOFs where a connectivity <12 of the clusters is observed. Although \(\text{H}_2\text{O}, \text{OH}^-, \text{and O}^{2-}\) groups cannot be distinguished from the PXRD data, based on the available data and the structure of the hexanuclear clusters, we propose the following sum formula \([\text{Zr}_6(\mu_1\text{-O})(\mu_2\text{-OH})_2(\text{H}_2\text{O})_3(\text{PzDC})_3]^{2+}\) for CAU-22, which is also corroborated by additional characterization data.

In addition to the crystal structure analysis, CAU-22 was thoroughly characterised by various methods to confirm the composition and to evaluate the thermal and chemical stabilities as well as the porosity. Temperature dependent powder X-ray diffraction shows a thermal stability for CAU-22 up to approximately 270 °C (Fig. S5.1, ESI†). The thermogravimetric analysis indicates a stepwise weight loss up to 270 °C which is due to the loss of water molecules. The X-ray powder diffraction analysis shows the formation of the product up to 550 °C (Fig. S5.2, ESI†). The isotherms for the uptake and release of water and CO2 show hysteresis loops indicating that the porous structure of the material is present during the adsorption process (Figs. S5.3 and S5.4, ESI†).
and the elemental analysis (Fig. S5.3 and Table S5.2, ESI† respectively) are in good agreement with the postulated sum formula of the framework \([\text{Zr}_6(\mu_3-\text{O})(\mu_2-\text{OH})(\mu_2-\text{OH})_2(\text{H}_2\text{O})_2(\text{HCO}_2)_2(\text{PzDC})_6] \) but the determined amount of adsorbed water molecules differs to the hydrophilic properties of CAU-22. The presence of water molecules in the pores of CAU-22 is confirmed by IR-spectroscopy where a strong band centred at 3267 cm\(^{-1}\) is observed (Fig. S6.1, ESI†). The \(^1\)H NMR spectrum of the dissolved MOF verifies the molar ratio PzDC\(^2^-\) to formate ions of three to two (Fig. S7.1, ESI†). SEM micrographs of CAU-22 show that the particles consist of small platelets of approximately 0.25 \(\mu\)m in diameter, which are assembled to larger aggregates of octahedral morphology (Fig. S8.1, ESI†).

To determine the porosity of CAU-22 a sample was activated at 120 °C for 16 h under reduced pressure. The nitrogen sorption measurement was carried out at –196 °C. The isotherm shows a Type I behaviour, typical for microporous compounds (Fig. 5), with a small hysteresis (H4-type). The latter is typical for microporous aggregated samples (Fig. S3.6, ESI†). The specific surface area is 276 \(\text{m}^2\ \text{g}^{-1}\) and the micropore volume is 0.12 cm\(^3\) g\(^-1\) (determined at \(p/p_0 = 0.5\)). It is slightly smaller than the theoretical micropore volume of 0.17 cm\(^3\) g\(^-1\) calculated with the program Platon.\(^{39}\) CAU-22 is highly hydrophilic, as demonstrated by water vapour sorption measurements carried out at 25 °C (Fig. 5).

The water isotherm shows a steep increase at low relative humidity values and an absolute uptake of about 0.16 g \(\text{g}^{-1}\) CAU-22, which is in good agreement with the anticipated pore volume. Compared to UiO-66 (0.30 g \(\text{g}^{-1}\)) the absolute water uptake is decreased but the steep rise in the isotherm starts at much lower \(p/p_0\) values, which can be associated with the more hydrophilic properties of the linker compared to terephthalate ions in UiO-66. After the sorption measurements, the high crystallinity of the samples was demonstrated by powder X-ray diffraction (Fig. S9.2, ESI†).

In conclusion, we synthesised a new Zr-MOF denoted CAU-22 by a water-based synthesis route employing a soluble mixture of water and formic acid. The structure of CAU-22 contains a unique 1D IBU which is formed by edge-sharing of the well-known hexanuclear \([\text{Zr}_6(\mu_3-\text{O})(\mu_2-\text{OH})_2]\) clusters. It is permanently porous towards nitrogen and water and in contrast to UiO-66 CAU-22 is very hydrophilic which is due to the incorporation of pyrazinedicarboxylate ions as the linker. We anticipate that other linker molecules with similar functionalities will lead to the same IBU.

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Notes and references
1 J. A. Mason, M. Veenstra and J. R. Long, Chem. Sci., 2014, 5, 32–51.
2 J.-R. Li, R. J. Kupper and H.-C. Zhou, Chem. Soc. Rev., 2009, 38, 1477–1504.
3 P. Valvekens, F. Vermoortele and D. De Vos, Catal. Sci. Technol., 2013, 3, 1435–1445.
4 F. Jeremias, D. Frohlich, C. Janiak and S. K. Henninger, New J. Chem., 2014, 38, 1846–1852.
5 F. Ke, Y.-P. Yuan, L.-G. Qiu, Y.-H. Shen, A.-J. Xie, J.-F. Zhu, X.-Y. Tian and L.-D. Zhang, J. Mater. Chem., 2011, 21, 3843–3848.
6 H. Furukawa, K. E. Cordova, M. O’Keeffe and O. M. Yaghi, Science, 2013, 341, 974–986.
7 Y. Bai, Y. Dou, L.-H. Xie, W. Rutledge, J.-R. Li and H.-C. Zhou, Chem. Soc. Rev., 2016, 45, 2363–2367.
8 T. Devic and C. Serre, Chem. Soc. Rev., 2014, 43, 6907–6115.
9 M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick and U. Schubert, Eur. J. Inorg. Chem., 2006, 2838–2893.
10 J. H. Cava, S. R. Jakobsen, U. Olsbye, N. Guilou, C. Lamberti, S. Bordiga and K. P. Lillerud, J. Am. Chem. Soc., 2008, 130, 13850–13851.
11 V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, CrystEngComm, 2013, 15, 9572–9577.
12 G. Wißmann, A. Schaate, S. Lilienthal, I. Bremer, A. M. Schneider and P. Behrens, Microporous Mesoporous Mater., 2012, 152, 64–70.
13 B. Bucken, H. Reinsch, N. Reimer, I. Stassen, F. Vermoortele, R. Ameloot, N. Stock, C. E. A. Kirschkhoef and D. De Vos, Chem. Commun., 2014, 50, 10055–10058.
14 S. Biswas, J. Zhang, Z. Li, Y.-Y. Liu, M. Graywa, L. Sun, D. Volkmer and P. Van Der Voort, Dalton Trans., 2013, 42, 4730–4737.
15 M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilsen, C. Larabi, E. A. Quadrelli, F. Bonino and K. P. Lillerud, Chem. Mater., 2010, 22, 6632–6640.
16 V. Bon, I. Senkovska, I. A. Baburin and S. Kaskel, Cryst. Growth Des., 2013, 13, 1231–1237.
17 V. Bon, V. Senkovska, I. Senkovska and S. Kaskel, Chem. Commun., 2012, 48, 8407–8409.
18 H. Furukawa, F. Gándara, Y.-B. Zhang, J. Jiang, W. L. Queen, M. R. Hudson and O. M. Yaghi, J. Am. Chem. Soc., 2014, 136, 4369–4381.
19 W. Morris, B. Volosskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, Inorg. Chem., 2012, 51, 6443–6445.
20 M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z.-J. Wang and H.-C. Zhou, Angew. Chem., Int. Ed., 2014, 53, 815–818.
21 V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross and C. Serre, Angew. Chem., Int. Ed., 2012, 51, 9267–9271.
22 D. Peng, H.-L. Jiang, Y.-P. Chen, Z.-Y. Gu, Z. Wei and H.-C. Zhou, Inorg. Chem., 2013, 52, 12661–12667.
23 M. Tuddel, F. Costantini, F. Marmottini, A. Comotti, P. Sozzani and R. Rivani, Chem. Commun., 2014, 50, 14831–14834.
24 G. Mouchaham, L. Cooper, N. Guilou, C. Martineau, E. Elkaïm, S. Bourrellé, P. L. Llewellyn, C. Allain, G. Clavier, C. Serre and T. Devic, Angew. Chem., Int. Ed., 2015, 54, 13297–13301.
25 Z. Hu, Y. Peng, Z. Kang, Y. Qian and D. Zhao, Inorg. Chem., 2015, 54, 4862–4868.
26 H. Reinsch, S. Waitschat, S. M. Chavan, K. P. Lillerud and N. Stock, Eur. J. Inorg. Chem., 2016, DOI: 10.1002/ejc.201600295.
27 F. Ragon, B. Campo, Q. Yang, C. Martineau, A. D. Wiersum, A. Lago, V. Guillerm, C. Hemsley, J. F. Eubank, M. Vishnuvarthan, F. Taulelle, P. Horcajada, A. Vimont, P. L. Llewellyn, M. Daturi, S. Devautour-Vinot, G. Maurin, C. Serre, T. Devic and G. Clet, J. Mater. Chem. A, 2015, 3, 3294–3309.
28 Q. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. Zhong, C. Serre,
G. De Weireld and G. Maurin, Angew. Chem., Int. Ed., 2013, 52, 10316–10320.
29 H. Reinsch, B. Bueken, F. Vermoortele, I. Stassen, A. Lieb, K.-P. Lillerud and D. De Vos, CrystEngComm, 2015, 17, 4070–4074.
30 H. Reinsch, Eur. J. Inorg. Chem., 2016, DOI: 10.1002/ejic.201600286.
31 W. J. Schut, H. I. X. Mager and W. Berends, Recl. Trav. Chim. Pays-Bas, 1961, 80, 391–398.
32 R. Plessius, R. Kromhout, A. L. D. Ramos, M. Ferbinteanu, M. C. Mittelmeijer-Hazeleger, R. Krishna, G. Rothenberg and S. Tanase, Chem. – Eur. J., 2014, 20, 7922–7925.
33 R. Cai, P. Yang, J.-W. Dai and J.-Z. Wu, CrystEngComm, 2011, 13, 985–991.
34 N. Stock and S. Biswas, Chem. Rev., 2012, 112, 933–969.
35 A. Topas Academics 4.2, Coelho Software, Brisbane, 2007.
36 A. Altomare, M. Camalli, C. Cuocci, C. Giacovazzo, A. Moliterni and R. Rizzi, J. Appl. Crystallogr., 2009, 42, 1197–1202.
37 C. Materials Studio Version 5.0, Accelrys Inc., San Diego, 2009.
38 M. Thommes, K. Kaneko, V. Neimark Alexander, P. Olivier James, F. Rodriguez-Reinoso, J. Rouquerol and S. W. Sing Kenneth, Pure Appl. Chem., 2015, 87, 1051.
39 A. Spek, Acta Crystallogr., 2009, 65, 148–155.