Zn(II) metal–organic framework with dinuclear [Zn_2(*N*-oxide)$_2$] secondary building units

Journal:	*Dalton Transactions*
Manuscript ID	DT-COM-12-2018-004879.R1
Article Type:	Communication
Date Submitted by the Author:	19-Feb-2019
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Journal Name

COMMUNICATION

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We report the synthesis, structural characterisation, and adsorption properties of a three-dimensional metal–organic framework [Zn(pydcao)(DMF)] (H_2-pydcao = 3,5-pyridinedicarboxylic acid *N*-oxide) that has an unprecedented [Zn_2(*N*-oxide)$_2$] secondary building unit.

Metal–organic frameworks (MOFs) constructed from metal nodes and organic bridging ligands have attracted much attention as functional materials possessing catalytic,[1] conductive,[2] optical,[3] magnetic[4] and porosity-associated[5] properties. MOFs have unlimited potential due to their high structural regularity and diversity, the simplicity of framework modification and the high degree of freedom of their electronic states.[6] When designing the synthesis of a new class of MOFs, an important concept to keep under consideration is that of the secondary building unit (SBU), as this unit's geometric and chemical characteristics can be exploited to obtain MOFs with desired structural and/or functional traits.[7] For example, MOFs with unprecedented chemical and thermal stability have been obtained using Zr_6 clusters as SBUs.[8] Therefore, SBU design is an effective approach to obtaining new framework topologies. Various SBUs have been synthesised to date, including paddle-wheel dimer units,[9] a tetrahedral [Zn_4(O)] cluster[10] and Zr clusters.[11] In particular, the paddle-wheel [M_2L_4] (M = metal cation; L = organic bridging ligand) units, comprising two metal cations bridged by four carboxylate groups, are widely known as dimer-type SBUs that form four-connected and six-connected nodes.

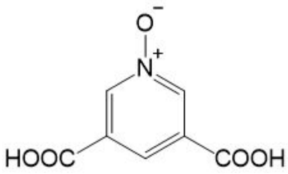

Fig. 1 Chemical structure of 3,5-pyridinedicarboxylic acid *N*-oxide.

Herein, we report the synthesis, structural characterisation, and adsorption properties of the three-dimensional (3D) Zn(II) MOF [Zn(pydcao)(DMF)] (**1**·DMF) (H_2-pydcao = 3,5-pyridinedicarboxylic acid *N*-oxide; Fig. 1). Two pyridine *N*-oxide moieties have been reported to bridge two metal cations, resulting in the formation of a discrete dimer [M_2(*N*-oxide)$_2$] (M = Cu,[12] Mn[13] or Cd[14]). In the present study, we have, for the first time, used [M_2(*N*-oxide)$_2$] clusters as SBUs of MOFs.

The reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with H_2-pydcao·H_2O[15] in *N*,*N*-dimethylformamide (DMF) yielded the 3D MOF **1**·DMF (see ESI†). Single-crystal X-ray diffraction (XRD) data indicate that **1**·DMF crystallizes in a monoclinic $P2_1/c$ space group (Table 1). The asymmetric unit contains one Zn(II) cation, one pydcao^{2-} ligand and one coordinated DMF molecule. Zn(II) is coordinated by two η^1-oxygen atoms of the carboxylate groups, two η^2-oxygen atoms of the *N*-oxide group of two pydcao^{2-} ligands and one oxygen atom of the DMF molecule (Fig. 2a). The resulting coordination environment is that of a distorted square pyramid with $\tau = 0.10$.[16] The N^+–O^- bond distance in the pydcao^{2-} ligand (1.351(2) Å) is slightly longer than that of its counterpart in crystalline non-coordinating neutral H_2-pydcao (1.336(4) Å).[15] This difference is the result of the accumulation of further negative charge on the *N*-oxide oxygen atoms caused by the coordination of the divalent Zn(II) cations. In fact, this charge accumulation enhances the single-bond character of the N^+–O^- bond. The Zn–O(N^+–O^-) bond distances (2.088(1) and 2.113(1) Å) are longer than the Zn–O(COO^-) bond distances (1.964(1) and 1.969(1) Å). The pydcao^{2-} ligand displays a μ_4-coordination

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†Electronic Supplementary Information (ESI) available: Synthesis of compounds and measurements (Figs S1–S5). CCDC: 1564018. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

Table S1. Crystallographic data for [Zn(pydcao)(DMF)].

Formula	$C_{10}H_{10}O_6N_2Zn$
Formula weight	319.57
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	7.9070(5)
b / Å	15.2244(8)
c / Å	10.2954(7)
β / deg.	91.868(2)
V / Å^3	1238.69(13)
Z	4
Crystal size / mm^3	0.20 × 0.15 × 0.08
T / K	173
D_c / g cm^{-3}	1.714
F_{000}	648
λ / Å	0.71075
μ (Mo Kα) / mm^{-1}	0.374
R_1 [$I > 2.00\sigma(I)$][a]	0.0259
R (all reflections)[a]	0.0331
wR_2 (all reflections)[b]	0.0703
GOF	1.101
Number of observations	2811
Number of variables	2431
CCDC number	1564018

[a] $R_1 = R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [(\Sigma w(|F_o|^2 - |F_c|^2)^2)/\Sigma w(F_o{}^2)^2]^{1/2}$.

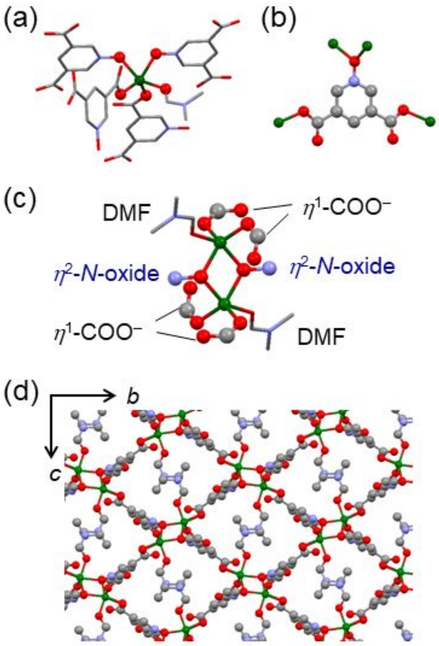

Fig. 2 Crystal structure of [Zn(pydcao)(DMF)] (**1**·DMF). (a) Coordination environment around the Zn(II) cation, (b) coordination mode of the pydcao^{2-} ligand, (c) coordination environment around the [Zn_2(*N*-oxide)$_2$] SBU, and (d) 3D structure of 1·DMF. Green represents zinc; red, oxygen; blue, nitrogen; and gray, carbon. Hydrogen atoms are omitted for clarity.

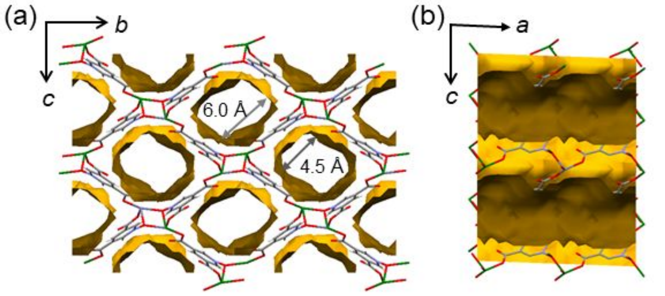

Fig. 3 1D pore structure of [Zn(pydcao)] projected along the (a) *a* axis and (b) *b* axis, in which the probe with the radius of 1.2 Å was used to trace the pore structure.

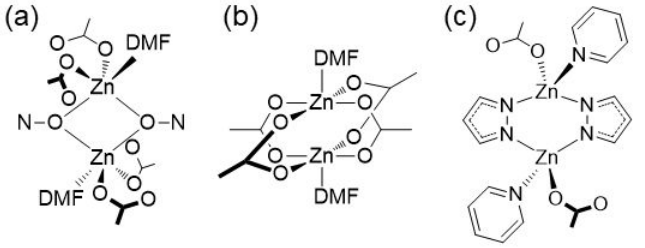

Fig. 4 Structures of Zn_2 SBUs. (a) [Zn_2(*N*-oxide)$_2$] SBU of **1**·DMF, (b) [$Zn_2(COO)_4$] SBU of [Zn(bdc)(DMF)][18] and (c) [Zn_2(pyrazolate)$_2$] SBU of {[$Zn_2(pzca)_2$(4,4′-bpy)]·$2H_2O$}.[19]

mode with one η^2-oxygen of the pyridine-*N*-oxide group and two η^1-oxygens of the two carboxylate groups (Fig. 2b). Two *N*-oxide-based η^2-oxygens coordinate two Zn(II) cations at once to form a dinuclear [Zn_2(*N*-oxide)$_2$] SBU, whereby the Zn–Zn distance is 3.421 Å and the Zn–O–Zn bond angle is 109.01(6)° (Fig. 2c). To the best of our knowledge, this is the first MOF that includes [M_2(*N*-oxide)$_2$] SBUs. The six-connected [M_2(*N*-oxide)$_2$] SBUs are linked together through the three-connected pydcao^{2-} ligand to form a 3D structure characterised by one-dimensional (1D) channels (Fig. 2c and 3). These channels with approximate dimensions of *ca.* 4.5 Å × 6.0 Å are occupied by DMF molecules that coordinate with the metal ions to form 2.083-Å-long Zn–O bonds. The solvent-accessible volume calculated for the desolvated **1** using PLATON (probe radius: 1.2 Å) is 38.9%.[17]

In the two-dimensional MOF [Zn(bdc)(DMF)] (bdc^{2-} = 1,4-benzenedicarboxylate) reported by Brammer *et al.*, the traditional paddle-wheel [$Zn_2(COO)_4$] SBUs form during crystallisation.[18] Recently, the 3D MOF {[$Zn_2(pzca)_2$(4,4′-bpy)]·$2H_2O$} (pzca^{2-} = a deprotonated form of 1*H*-pyrazole-4-carboxylic acid, 4,4′-bpy = 4,4′-bipyridine) with [Zn_2(pyrazolate)$_2$] SBUs has been synthesised by Zhao *et al.*.[19] As is the case with [Zn_2(*N*-oxide)$_2$], these SBUs are characterised by a dimeric structure. The structures of these three types of Zn_2 SBUs are illustrated in Fig. 4. In the [$Zn_2(COO)_4$] SBU, the dimeric structure is generated by four carboxylate moieties coordinating the Zn(II) cations, whereas two *N*-oxide and two pyrazolate groups are the building blocks of the SBUs in **1**·DMF and {[$Zn_2(pzca)_2$(4,4′-bpy)]·$2H_2O$}, respectively. The Zn–Zn distance of the [Zn_2(*N*-oxide)$_2$] SBU (3.421 Å) is considerably

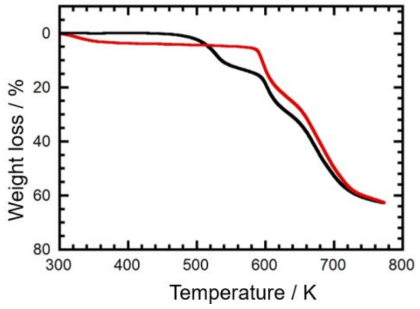

Fig. 5 TG curves of the (a) as-synthesized **1**·DMF and (b) the desolvated **1** obtained by drying the as-synthesized **1**·DMF under vacuum at 478 K for 4 hours.

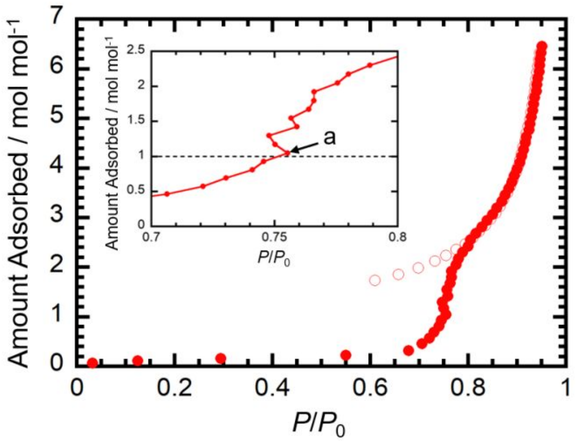

Fig. 6 Adsorption (closed circles) and desorption (open circles) isotherms of the desolvated **1** for H_2O at 298 K. Inset: H_2O adsorption isotherm at around point a.

longer than that of the [$Zn_2(COO)_4$] SBU (2.951(1) Å), and it is similar to that of the [Zn_2(pyrazolate)$_2$] SBU (3.480 Å). Although the [Zn_2(*N*-oxide)$_2$] and [Zn_2(pyrazolate)$_2$] SBUs have similar structural characteristics, a notable difference between them lies in the fact that the metal-connecting moieties of the former are neutral, whereas those of the latter are monoanionic. The structural differences between these three Zn_2 SBUs mean that the [Zn_2(*N*-oxide)$_2$] SBU synthesised in this study may be a good candidate for the generation of novel porous frameworks.

The framework stability of **1**·DMF was evaluated by thermogravimetric (TG) and powder XRD analysis. TG evidence (Fig. 5) indicates that **1**·DMF loses 23% of its weight between 420 K and 515 K, suggesting that in this temperature range **1**·DMF loses one DMF molecule per formula unit (~22.9%). The framework decomposition of the desolvated **1** is observed at ~580 K.

To verify that the porous structure had been maintained after the removal of the coordinated DMF molecules from **1**·DMF, the powder XRD pattern of the desolvated **1**, obtained by drying the as-synthesised **1**·DMF under vacuum at 478 K for 4 hours (see ESI†), was measured. The powder XRD pattern of the desolvated **1** is characterised by sharp peaks in similar positions as those of the as-synthesised **1**·DMF (Fig. S1, ESI†), indicating that the 3D porous framework is maintained after DMF removal. The appearance of the TG curve of the desolvated **1** also supports the conclusion that the DMF molecules had been removed (Fig. 5). Temperature-dependent powder XRD patterns were also measured under vacuum (Fig. S2, ESI†). Up to a temperature of 493 K, the powder XRD patterns remained almost unchanged; at 533 K, however, the intensity of the lowest-angle peak decreased considerably, suggesting that framework porosity is retained up to at least 493 K.

To investigate the fundamental properties of the pores of desolvated **1**, the adsorption/desorption isotherms for N_2 (77 K), CO_2 (195 K) and H_2 (77 K) were measured (Fig. S3, ESI†). All gases are hardly adsorbed onto the desolvated **1.** The BET surface area calculated from the N_2 adsorption isotherm is 2.5 $m^2 \cdot g^{-1}$. Although the smaller dimension of the 1D channels (4.5 Å) is larger than the kinetic diameters of N_2 (3.6 Å), CO_2 (3.3 Å) and H_2 (2.9 Å), the void calculation was performed using the probe radius of 1.2 Å, which is considerably smaller than the kinetic diameters just mentioned. If we use a probe radius of 2.5 Å, the solvent-accessible volume becomes 0%. This result implies that the desolvated **1** has no valid accessible void for the gases used in the sorption experiments.

The TG curve of the desolvated **1** in Fig. 5 showed a weight loss of 4.35 % in the temperature region between 300 and 493 K, which is due to a small uptake of atmospheric water and corresponds to 0.62 mol of water per 1 mol of **1**. This means that the desolvated **1** may adsorb water with retention of the original framework. We therefore measured the H_2O adsorption/desorption isotherms of **1** at 298 K. As shown in Fig. 6, the adsorbed amount of H_2O was gradually increased up to 1.1 $mol \cdot mol^{-1}$ at $P/P_0 = 0.76$ (point a in Fig. 6), which almost agrees with the number of coordinatively unsaturated sites of the desolvated **1** (1 $mol \cdot mol^{-1}$). At the next measurement point, the equilibrium pressure was smaller than last one, which is characteristic of porous materials showing an adsorption with a structural change.[20] After that, the adsorption amount was sharply increased up to 6.6 $mol \cdot mol^{-1}$ at $P/P_0 = 0.95$. In the desorption process, a hysteresis was observed. The powder XRD patterns after the adsorption/desorption measurement were completely different from the simulated pattern (Fig. S4, ESI†). From these results, we propose the adsorption/desorption mechanism as follows: In the adsorption process, the desolvated **1** adsorbs water on the coordinatively unsaturated sites up to 1 $mol \cdot mol^{-1}$ without marked structural change. Plausible reasons for such water adsorption behavior could be (1) the smaller kinetic diameter (2.65 Å) than those of N_2 (3.6 Å), CO_2 (3.3 Å) and H_2 (2.9 Å), (2) the accelerating guest diffusion at higher measurement temperature (298 K), and/or (3) the coordination of water to the coordinatively unsaturated sites. After filling their sites, water molecules start to destroy the framework because of the instability of Zn(II) MOFs in humid environments.[21] Consequently, the original porous structure is not recovered after the removal of adsorbed water molecules from the water-exposed sample.

Conclusions

We succeeded in synthesising the 3D MOF [Zn(pydcao)(DMF)] using the dinuclear [Zn_2(*N*-oxide)$_2$] cluster as SBU. The obtained framework was stable after the removal of guest DMF molecules and showed water adsorption on the coordinatively unsaturated sites. We believe that this SBU will contribute to the generation of MOFs with novel topological and functional characteristics. Further material development is now ongoing in our research group using organic ligands with *N*-oxide moieties other than those of H_2-pydcao.

Acknowledgements

This work was supported by the ‘ACCEL Project’ (JPMJAC1302) from the Japan Science and Technology Agency and Creative Research Institution, Hokkaido University, Japan. We thank Ms. Ai Tokumitsu and Ms. Yukako Sasaki (Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University, Japan) for carrying out elemental analyses. We acknowledge Dr. Hiroyasu Sato (Rigaku Corporation) for assistance with single-crystal X-ray diffraction analysis.

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Graphical Abstract

A three-dimensional metal organic framework with unprecedented $[Zn_2(N\text{-oxide})_2]$ secondary building units was synthesized using 3,5-pyridinedicarboxylic acid *N*-oxide.