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New microporous coordination polymer affording guest-coordination sites at channel walls†

Shin-ichiro Noro,[a,b] Susumu Kitagawa,*[a] Masahiro Yamashita[c] and Tatsuo Wada[b]

[a] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan. E-mail: kitagawa@sbchem.kyoto-u.ac.jp*

[b] *RIKEN (The Institute of Physical and Chemical Research), 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan*

[c] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji-shi, Tokyo 192-0397, Japan*

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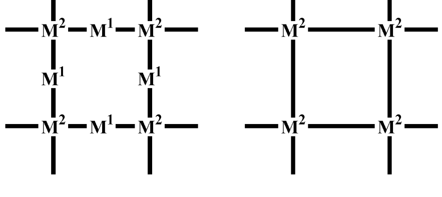
Utilization of a metalloligand, {[Cu(2,4-pydca)$_2$(H$_2$O)]·2Et$_3$NH} (1) (2,4-pydca = pyridine-2,4-dicarboxylate), as a building unit provides a novel porous coordination polymer, {[ZnCu(2,4-pydca)$_2$(H$_2$O)$_3$(DMF)]·DMF}$_n$ (2), in which the Zn(II) ion at the node of the network acts as a linker and the Cu(II) ion in the channel wall is available for guest-coordination.

Porous coordination polymers are of great interest due to their unique properties such as adsorption,[1–3] ion-exchange,[4] and heterogeneous catalysis.[5] In particular, if coordinatively unsaturated metal ions can be incorporated not in nodal sites but in channel walls, new porous properties would be created on the basis of coordination of guest molecules.[6–8] However, the synthesis of such compounds by "one-step self-assembly" method is very difficult because metal ions tend to occur in nodes of frameworks and therefore all the coordination sites are occupied by bridging ligands and/or counter anions (Scheme 1, right). In order to create a porous framework containing coordinatively unsaturated metal centers, we developed a new synthetic scenario denoted 'two-step self-assembly'. First, a metalloligand is synthesized which acts as not only a framework linker but also a coordinatively unsaturated metal center (M^1). Second, the metalloligand is added to another metal ion (M^2), which acts as a nodal unit of a framework. Consequently, two kinds of metal centers coexist in a framework (Scheme 1, left), and a larger space around the metal ion at the channel wall can be obtained, relevant for incorporation of guest molecules.

The metalloligand **1** was obtained from the reaction of CuSO$_4$·5H$_2$O with 2,4-H$_2$pydca and Et$_3$N in the mixed solvent H$_2$O–MeOH. Crystals suitable for X-ray analysis of **2** were prepared by reaction of Zn(NO$_3$)$_2$·6H$_2$O with **1** in hot DMF.‡

An ORTEP view around metal centers of **2** is shown in Fig. 1(a). In the crystal, there are three crystallographically independent metal centers, Cu(1), Cu(2) and Zn. Each Cu(II) atom lying on independent inversion centers is based on an elongated octahedral environment with the two oxygen atoms and the two nitrogen atoms of 2,4-pydca^{2-} ligands in the equatorial plane, and the two oxygen atoms of H$_2$O and DMF molecules at the axial positions for Cu(1) and Cu(2), respectively. On the other hand, the Zn(II) center shows a distorted octahedron with the three oxygen atoms of H$_2$O molecules, the two oxygen atoms of the 4-carboxylate in a semi-chelating fashion,[9,10] and the oxygen atom of another 4-carboxylate in a monodentate fashion. The O–Zn–O bond angles for *trans* and *cis* orientation range from 152.2(1) to 177.7(1)°, and 59.0(1) to 104.0(1)°, respectively. It is worth noting that the coordination environment of **1** used as a building block is retained even in the



Scheme 1

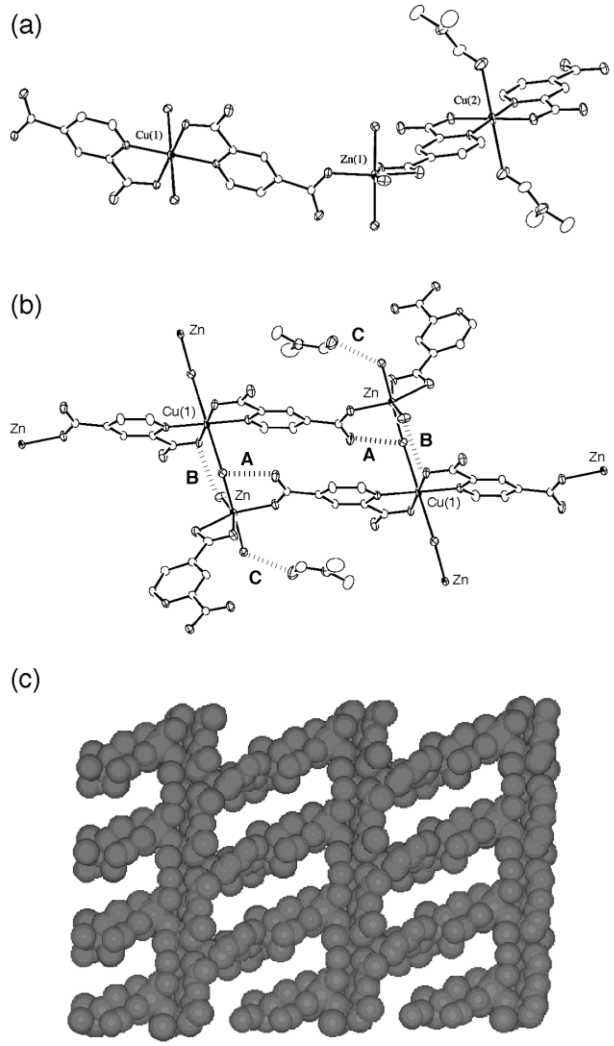


Fig. 1 (a) ORTEP drawing around metal centers of **2** at the 30% probability level. The hydrogen atoms are omitted for clarity. (b) ORTEP drawing of a bridging mode between 1-D chains of **2**. The dotted line represents a hydrogen bond. The hydrogen atoms are omitted for clarity. (c) View of a microporous network of **2** along the *c*-axis. The guest DMF molecules and the hydrogen atoms are omitted for clarity.

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† Electronic supplementary information (ESI) available: Fig. S1: XRPD patterns of (a) simulation, (b) **2** and (c) **3**. See http://www.rsc.org/suppdata/cc/b1/b108695b/

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extended structure. As a result, the ligand 2,4-pydca^{2-} shows a characteristic coordination feature in the framework; the carboxylate group at 2-position for both Cu(II) ions is involved in a chelating mode together with the nitrogen atom while that at 4-position is coordinated only to Zn(II) ion, adopting semi-chelating and monodentate coordination modes.

The 2,4-pydca^{2-} ligands bridge the Cu and Zn ions alternately to provide an undulated 1-D chain structure of ···Zn–Cu(2)–Zn–Cu(1)–Zn–Cu(2)···, in which the Cu(1)–Zn–Cu(2) angle is 116°. The intrachain distances of Cu(1)–Zn and Cu(2)–Zn are 8.90 and 8.75 Å, respectively. As shown in Fig. 1(b), these chains are linked by H_2O molecules, which bridge between the Zn and Cu(1) ions (Zn–O 2.178(3) Å, Cu(1)–O 2.713(3) Å).[11] The bridging H_2O molecules are also supported by 4-carboxylates (hydrogen bond A: O···O 2.665(4) Å). In addition, their chains are connected *via* hydrogen bonds between coordinated H_2O molecules at the Zn centers and the oxygen atoms of 2-carboxylates (hydrogen bond B: O···O 2.818(4) Å). These two linkages create a 2-D network of a large grid. Each sheet is linked to adjacent ones by hydrogen bonds among coordinated H_2O molecules at the Zn centers and the oxygen atoms of 2- and 4-carboxylates (av. 2.740 Å) to form rhombic cavities with a dimension of *ca.* 15 × 5 Å as shown in Fig. 1(c). These cavities are filled with two types of DMF molecules. One is weakly coordinating to the Cu(2) center (Cu(2)–O 2.513(4) Å), and the other is connected to a coordinated H_2O molecule at the Zn(II) center *via* a hydrogen bond (hydrogen bond C: O···O 2.662(5) Å) as illustrated in Fig. 1(b).

There are eight metal units per cavity as illustrated in Fig. 2. The two Cu(1) units act only as a node. On the other hand, the Cu(2) units are located on both sides of the cavity, accompanying DMF molecules at the axial sites. The four Zn sites are coordinatively saturated, essentially located in nodal positions but provide one of the coordinated water molecules as a hydrogen bond donor/acceptor toward the channel cavity. Therefore, the residual DMF molecules are trapped by a hydrogen bond. As compared with the Zn sites at the nodal positions, the Cu(2) ions at channel walls have enough space to trap larger guest molecules at the axial sites.

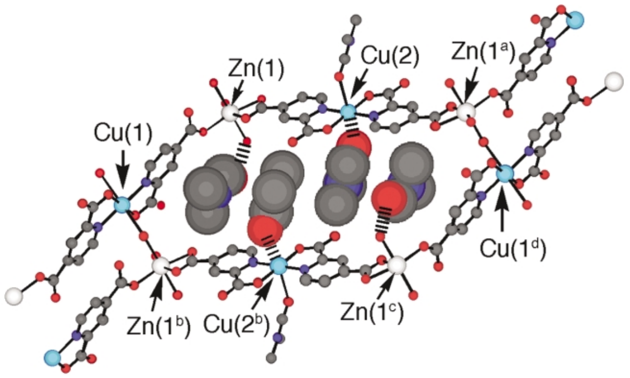

Fig. 2 View of one cavity of **2**. The guest DMF molecules are represented by a space filling model. The hydrogen atoms are omitted for clarity. Symmetry code: $^a-x, -y+1, -z+2$. $^b x+1, y, z+1$. $^c -x+1, -y+1, -z+3$. $^d x-1, y+1, z+1$.

Compound **2** was immersed in a H_2O solution for one day, subsequently filtered and dried under vacuum. The resulting compound, $\{[ZnCu(2,4\text{-pydca})_2(H_2O)_4]\cdot xH_2O\}_n$ (**3**), shows that all the DMF molecules are replaced with H_2O. Compound **3** shows high crystallinity during the guest exchange process as indicated by sharp peaks observed in the XRPD pattern. The pattern is, however, slightly different from that of **2**. This observation shows that the cavity of **2** is so flexible that H_2O molecules may be incorporated instead of DMF molecules without collapse or decomposition.

In conclusion, we succeeded in obtaining a novel porous coordination polymer **2** by a two step synthesis with the aid of the metalloligand, which could be relevant for chemical modification of channel cavities.

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Notes and references

‡ *Crystal data* for **2**: $C_{20}H_{26}CuN_4O_{13}Zn$, M = 659.37, triclinic, space group $P\bar{1}$ (no. 2), a = 10.5857(9), b = 20.308(2), c = 6.3289(6) Å, α = 92.801(4), β = 107.034(4), γ = 92.175(5)°, V = 1297.3(2) Å^3, T = 296 K, Z = 2, μ(Mo-Kα) = 18.17 cm^{-1}, 11493 reflections measured, 5752 unique (R_{int} = 0.049) which were used in all calculations. $R1$ = 0.048 (I = 2.00$\sigma(I)$), R_w = 0.116 (all data). CCDC reference number 168984. See http://www.rsc.org/suppdata/cc/b1/b108695b/ for crystallographic data in CIF or other electronic format.

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