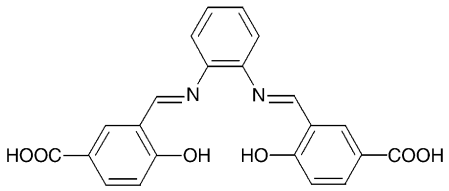
Crystal Engineering

Immobilization of a Metallo Schiff Base into a Microporous Coordination Polymer**

*Ryo Kitaura, Goro Onoyama, Hirotoshi Sakamoto, Ryotaro Matsuda, Sin-ichiro Noro, and Susumu Kitagawa**

Immobilization of coordinatively unsaturated metal centers (UMCs) into porous frameworks is a very attractive area of research because the porous framework can induce regioselectivity or shape/size selectivity by creating an appropriate environment around the metal center in the restricted available space. Furthermore, porous frameworks can stabilize the catalytic center by efficiently isolating the sites in a manner similar to the peptide architecture of enzymes in biological systems. Immobilization of UMCs into porous hosts has been attempted with zeolites, polymeric matrices, and clays through ion exchange, impregnation, and isomorphous substitution.[1,2] However, in these cases, the isolation and uniformity of the UMCs is not sufficient and the environment around the UMCs is not clear. Completely isolated and uniform catalytic centers can be realized if the UMCs are directly incorporated into channel walls of crystalline microporous coordination polymers constructed from transition-metal ions and organic bridging ligands.[3,4] Such a situation would lead to novel highly selective catalysts and sensors.

In spite of the importance, the incorporation of UMCs into porous frameworks is still rare because of difficulties associated with the formation of UMCs in channel walls by a self-assembly process.[5–7] Therefore, we focused on the establishment of a rational synthetic method to immobilize various UMCs in the pore walls of microporous coordination polymers. Ligands based on metallo Schiff bases are known to be useful for the generation of supramolecular systems for homogeneous catalyses and so might be suitable for incorporation into infinite porous frameworks for applications in heterogeneous catalyses and sensors.[8,9] Here, we report a novel three-dimensional (3D) microporous coordination framework obtained from Schiff base type ligands prepared from the reaction of *N*,*N*′-phenylenebis(salicylideneimine)dicarboxylic acid (H_4salphdc, Scheme 1) with Cu^{II}, Ni^{II}, and Co^{II} ions. These ligands play a key role as linkers with UMCs while Zn^{II} ions act as connectors of the framework. It should be noted that we can rationally immobilize different metal cations into the pore walls of a coordination framework to form complexes of the general form $[Zn_3(OH)_2(L^M)_2]$ (L^M = Schiff base type metalloligand $[M(salphdc)]^{2-}$, M = Cu^{II}, Ni^{II}, and Co^{II}) by using this synthetic method.



Scheme 1. Schematic representation of H_4salphdc.

In a typical synthesis, the reaction of $Cu(OAc)_2 \cdot H_2O$ and H_4salphdc in a DMF/MeOH/H_2O solution at room temperature results in brown needle crystals of $[Cu(H_2salphdc)] \cdot H_2O$. Figure 1 shows the coordination environment around the Cu^{II} ion of $[Cu(H_2salphdc)] \cdot H_2O$, together with the numbering scheme. The Cu^{II} ion is coordinated in a square-planer geometry with two nitrogen atoms and two oxygen atoms from the chelating salphdc ligand. The carboxylate groups of the salphdc ligands are not involved in the coordination to the Cu^{II} ion and, therefore, can be utilized for coordination to other metal centers. $[Cu(H_2salphdc)] \cdot H_2O$ is

[*] Dr. R. Kitaura,[+] G. Onoyama, H. Sakamoto, R. Matsuda, Dr. S.-i. Noro,[++] Prof. Dr. S. Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering
Kyoto University
Katsura, Nisikyo-ku, Kyoto 615-8510 (Japan)
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

[+] Current Address: Toyota Central R&D Laboratories, Inc.
Nagakute, Aichi, 480-1192 (Japan)

[++] Current Address: Supramolecular Science Laboratory
RIKEN (The Institute of Physical and Chemical Research)
2–1 Hirosawa, Wako-shi, Saitama, 351-0198 (Japan)

[**] This work was supported by a Grant-in-Aid for Creative Scientific Research (no. 13GS0024) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. The authors are most grateful to Dr. Masaaki Ohba and Wakako Kaneko for measuring the magnetic susceptibility of compound **3**.

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim DOI: 10.1002/ange.200352596

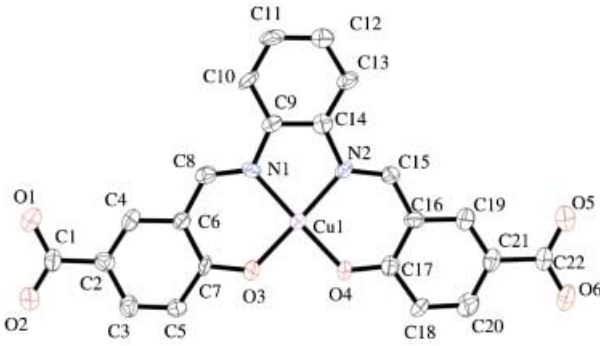


Figure 1. ORTEP drawing of [Cu(H_2salphdc)]·H_2O. Water molecules and hydrogen atoms are omitted for clarity.

soluble in DMF, DMSO, and pyridine and slightly soluble in MeOH.

The metalloligand [Cu(H_2salphdc)]·H_2O reacts with $Zn(NO_3)\cdot 6H_2O$ to afford a 3D coordination framework **1**·2 DMF ($[Zn_3(OH)_2(L^{Cu})_2]\cdot 2$ DMF). Figure 2a shows the coordination environments around the Cu^{II} and Zn^{II} ions of **1**·2 DMF. This crystal has two crystallographically independent Zn^{II} ions. One (Zn(1)) is tetrahedrally coordinated to two hydroxide anions and two carboxylate oxygen atoms of L^{Cu} and the other (Zn(2)) is octahedrally coordinated to two hydroxide anions and four carboxylate oxygen atoms of L^{Cu} to form an infinite chain structure. These chains are further linked by L^{Cu} to form a 3D porous structure, which possesses one-dimensional (1D) large channels with a cross-section of approximately 14×14 Å^2 (Figure 2b) and a large free void space of about 53% if the van der Waals radii of the constituting atoms are considered. Only one DMF molecule per Cu^{II} ion was determined by crystallography to be in the channel, and this is tightly anchored to the framework by a hydrogen bond with the carboxylate oxygen atom. The absence of other guest molecules in the channel of **1**·2 DMF was attributed to the disorder of included guest molecules as a result of the large channel size of **1**·2 DMF.

Interestingly, coordinatively unsaturated Cu^{II} ions line up along the *c*-axis with an intermetallic distance of 6.1 Å. To our knowledge, this is the first example of metallo Schiff base moieties being embedded regularly in the pore wall of a 3D porous framework. Although similar frameworks were reported with 4,4′-biphenyldicarboxylate and 2,6-naphthalenedicarboxylate,[10] the present porous structure with UMCs has added a new dimension to metal–organic framework chemistry. Bulk samples of this material are stable in air and are insoluble in common organic solvents. The IR spectrum of the material shows no absorptions bands characteristic of any protonated salphdc ligand, thus confirming complete deprotonation of [Cu(H_2salphdc)]. X-ray powder diffraction (XRPD) measurements with heating under reduced pressure were performed to examine the stability of the framework (Figure 3). The XRPD pattern of as-prepared **1** measured at

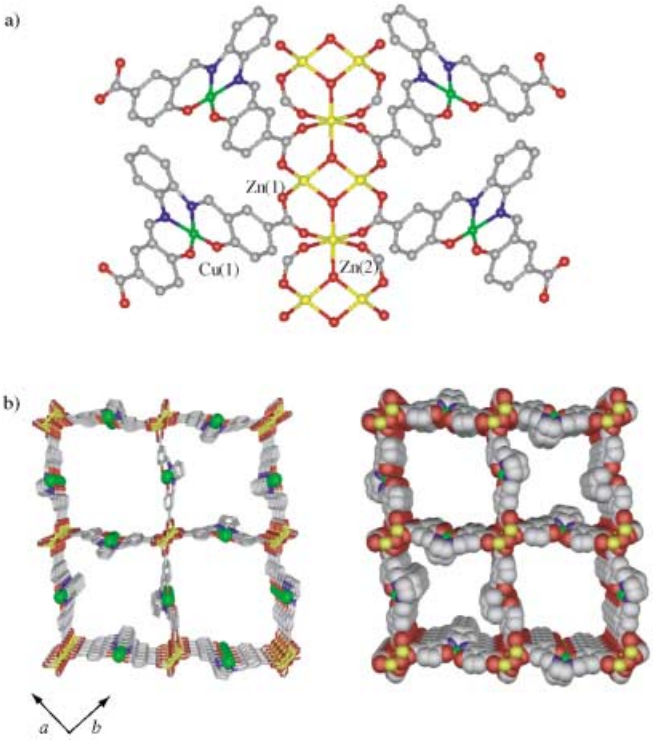


Figure 2. a) The building unit in the 3D porous coordination polymer, **1**·2 DMF. The hydrogen atoms and DMF molecule are omitted for clarity. b) 3D porous structure of **1**·2 DMF viewed down the *c*-axis (Zn, yellow; Cu, green; O, red; C, gray; N, blue). One of the doubly disordered phenylenediamine groups and the Cu atoms are omitted for clarity.

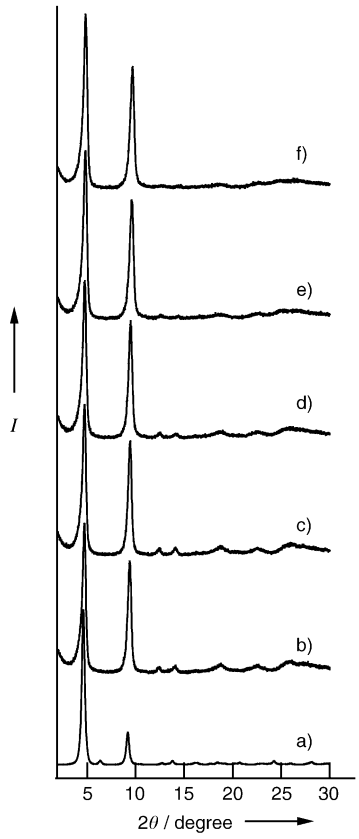


Figure 3. XRPD patters of as-synthesized **1** with heating from 298 to 523 K. a) Simulated pattern from single-crystal data and the b)–f) XRPD patterns at 298, 373, 423, 473, and 523 K, respectively.

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

298 K (Figure 3b) is in agreement with that of a simulated pattern obtained from the single-crystal structure (Figure 3a). The sharp peaks obtained over all the temperature regions investigated indicate that the crystallinity was retained. The patterns were almost the same: there was a slight shift in the peak positions from the original ones and a weakening of the peak intensities at higher angles. For example, two strong reflections, (110) and (220), were shifted to the higher angle region by 0.3 and 0.5°, respectively. Consequently, the porous structure was maintained with only slight structure distortions up to 573 K. A detailed study of these structural torsions is underway. We also investigated the use of Co^{II} and Ni^{II} ions instead of Cu^{II} ions to obtain other UMCs. The Co^{II}- and Ni^{II}-incorporated porous coordination polymers $[Zn_3(OH)_2(L^{Co})_2]_n$ (**2**) and $[Zn_3(OH)_2(L^{Ni})_2]_n$ (**3**) were also synthesized by a similar synthetic procedure to **1**. Figure 4 shows the

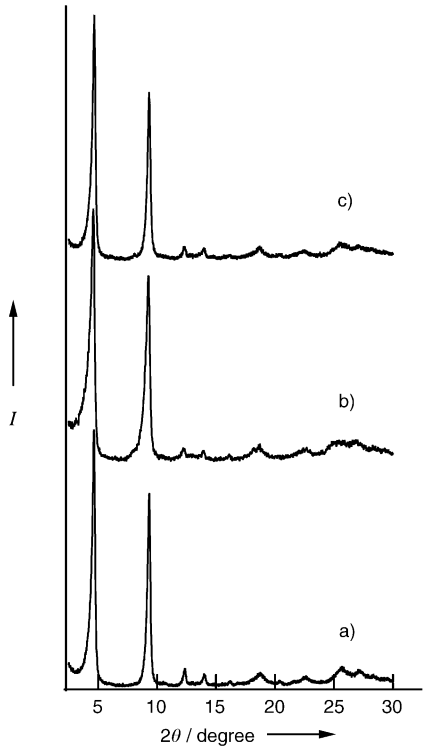


Figure 4. XRPD patters of a) as-synthesized **1**, b) **2** and c) **3**.

XRPD patterns of **2** and **3**.[11] The diffraction patterns are in good agreement with that of **1**, thus indicating that the 3D framework is isostructural and, hence indicates that coordinatively unsaturated Co^{II} and Ni^{II} ions had been successfully achieved.

This study demonstrates that completely uniform UMCs (Cu^{II}, Ni^{II}, and Co^{II}) can be embedded in the pore wall of a microporous coordination polymer by using the Schiff base type metalloligand $[M(salphdc)]^{2-}$ (L^M). This synthetic strategy could provide a new type of porous compound that could have applications in highly selective molecular recognition and heterogeneous catalysis.

Experimental Section

H_4salphdc: 3-Formyl-4-hydroxybenzoic acid (H_2fhba) was synthesized according to the literature procedure.[12] A solution of H_2fhba (1.08 g, 6.50 mmol) in EtOH (100 mL) was added dropwise to a solution of *o*-phenylenediamine (0.352 g, 3.25 mmol) in EtOH (100 mL) at 333 K. The orange powder precipitate of H_4salphdc was collected by filtration, washed with EtOH and THF, and dried under reduced pressure (1.11 g, 77%). ^{1}H NMR ([D$_6$]DMF): $\delta = 9.06$ (s, 2H), 8.33 (d, 2H), 7.95 (dd, 2H), 7.51 (m, 2H), 7.43 (m, 2H), 7.03 ppm (d, 2H).

$[Cu(H_2salphdc)]\cdot H_2O$: A solution of H_4salphdc (5 mM) in DMF/H_2O (4:1, 2.5 mL) was carefully layered on the top of a solution of $Cu(OAc)\cdot H_2O$ (5 mM) in DMF/MeOH (1:1, 2.5 mL). Brown needle-shaped crystals began to form in a few weeks. One of these crystals was used for X-ray crystallographic analysis. The bulk product was obtained by the following procedure. Slow addition of a solution of H_4salphdc (0.20 g, 1.2 mmol) in DMF (50 mL) to a solution of $Cu(OAc)\cdot H_2O$ (0.099 g, 1.2 mmol) in DMF (50 mL) provided a dark brown solution. Addition of MeOH to this dark brown solution resulted in precipitation of a brown powder of $[Cu(H_2salphdc)]\cdot H_2O$. The resulting brown powder was collected by filtration, washed with MeOH, and dried under vacuum for 2 h. Elemental analysis calcd for $C_{22}H_{16}CuN_2O_7$ (%): C 54.60, H 3.33, N 5.79; found: C 53.11, H 3.31, N 5.78; IR (KBr pellet): $\tilde{\nu} = 1668$s, 1605s, 1580s, 1529w, 1471w, 1414w, 1383s, 1300m, 1246s, 1191w, 1173w, 1134w, 953w, 843w, 776w, 753w, 696w, 649w, 533w cm^{-}.

1·2DMF: A solution of $[Cu(H_2salphdc)]\cdot H_2O$ (2.3 mg) in DMF (2.5 ml) was carefully layered on the top of a solution of $Zn(NO_3)_2\cdot 6H_2O$ (2.2 mg, 2.5 ml) in DMF/$CHCl_3$ (2 mL/0.5 mL). Brown needle-shaped crystals began to form in a few weeks. One of these crystals was used for X-ray crystallography. The bulk product was obtained by addition of a solution of H_4salphdc (0.098 g, 2.0 mmol) in DMF (100 mL) to a solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.089 g, 3.0 mmol) in DMF/H_2O (50 mL/15 mL) at 333 K. The brown powder obtained was collected by filtration, washed with DMF, and dried under vacuum for 5 h. There is an inherent difficulty in determining the number of guest molecules in such large open structures (**1**) because of disorder of guest molecules, their volatility, and the possibility of exchange. IR (KBr pellet): $\tilde{\nu} = 1612$s, 1580s, 1472m, 1422w, 1389s, 1357m, 1319m, 1242w, 1191m, 1129m, 958w, 846w, 786m, 752m, 706w, 657w, 557w cm^{-}.

2: This complex was prepared by a similar procedure as **1**, but using $Co(OAc)_2\cdot 4H_2O$. IR (KBr pellet): $\tilde{\nu} = 1613$s, 1562s, 1510w, 1467w, 1428m, 1392s, 1355m, 1323m, 1248w, 1197m, 1132m, 842w, 786s, 744m, 710w, 661w cm^{-}.

3: This complex was prepared by a similar procedure as **1** but using $Ni(OAc)_2\cdot 4H_2O$. IR (KBr pellet): $\tilde{\nu} = 1615$s, 1564s, 1506w, 1471w, 1431m, 1401s, 1359s, 1332m, 1251w, 1204w, 1135m, 842w, 814w, 786m, 744m, 712w, 664w cm^{-}.

Physical measurements: XRPD data were collected on a Rigaku RINT 2000Ultima diffractometer by using CuKα radiation. Elemental analyses were measured on a Yanaco C,H,N Corder MT-5. IR spectra were recorded on a Hitachi I-5040FT-IR spectrometer with samples prepared as KBr pellets.

X-ray structure determination: X-ray structure determinations were made on a Rigaku Mercury charge-coupled device (CCD) system with graphite monochromated MoK_α radiation. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure Corporation. $[Cu(H_2salphdc)]\cdot H_2O$: Crystal data: $C_{22}H_{12}CuN_2O_7$, $M_r = 479.89$, monoclinic, space group $P2_1/c$ (no. 14), $a = 16.05(2)$, $b = 7.286(7)$, $c = 18.86(2)$ Å, $\beta = 93.39(1)°$, $V = 2201(3)$ Å^3, $T = 223.2$ K, $Z = 4$, $\rho_{calcd} = 1.448$ g cm^{-3}, $\lambda(MoK_\alpha) = 0.71069$ Å, $2\theta_{max} = 55.00°$, 4898 reflections measured, 3235 observed ($I > 3.00\,\sigma(I)$), 284 parameters; $R = 0.0799$, $R_w = 0.1268$. **1**·2DMF: Crystal data: $C_{50}H_{40}Cu_2N_6O_{16}Zn_3$, $M_r = 1304.1$, monoclinic, space group $C2/m$ (no. 12), $a = 27.96(2)$, $b = 26.62(2)$, $c = 6.101(4)$ Å, $\beta = 94.96(1)°$, $V = 4523(5)$ Å^3, $T = 293.1$ K, $Z = 2$, $\rho_{calcd} = 0.962$ g cm^{-3},

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

$2\theta_{max} = 54.98°$, 5119 reflections measured, 1188 observed ($I > 3.00\,\sigma(I)$), 141 parameters; $R = 0.0996$, $R_w = 0.1255$. This framework possesses the disordered phenylenediamine group and the Cu atom (C1–C6, H1–H5, N1, N2, and Cu1). Therefore, the structure refinement was performed with occupancies of these atoms being half. CCDC-216654 and CCDC-216655 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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 deposit@ccdc.cam.ac.uk).

Received: August 7, 2003
Revised: March 3, 2004 [Z52596]

Keywords: coordination polymers · crystal engineering · materials science · N,O ligands · porous materials

[1] A. C. Sharma, A. S. Borovik, *J. Am. Chem. Soc.* **2000**, *122*, 8946–8955.
[2] G. A. Ozin, C. Gil, *Chem. Rev.* **1989**, *89*, 1749–1764.
[3] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem.* **2003**, *115*, 444–447; *Angew. Chem. Int. Ed.* **2003**, *42*, 428–431.
[4] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330.
[5] B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 11559–11560.
[6] S. Noro, S. Kitagawa, M. Yamashita, T. Wada, *Chem. Commun.* **2002**, 222–223.
[7] M. Kosal, J.-H. Chou, S. R. Wilson, K. S. Suslick, *Nat. Mater.* **2002**, *1*, 118–121.
[8] B. Moulton, M. Zawarotoko, *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 117–123.
[9] G. A. Morris, S. T. Nguyen, J. T. Hupp, *J. Mol. Catal. A* **2001**, *174*, 15–20.
[10] N. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2002**, *114*, 294–297; *Angew. Chem. Int. Ed.* **2002**, *41*, 284–287.
[11] The effective magnetic moment of compound **3** ($[Zn_3(OH)_2(L^{Ni})_2]_n$) at 300 K was 4.06 BM, which indicates that the axial sites of the Ni^{II} ions could be occupied by solvent molecules.
[12] N. Hofslokken, L. Skattebol, *Acta Chem. Scand.* **1999**, *53*, 258–262.

 © 2004 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim