$[Co_5(im)_{10}\cdot 2MB]_\infty$: A Metal-Organic Open-Framework with Zeolite-Like Topology**

Yun-Qi Tian, Chen-Xin Cai, Yong Ji, Xiao-Zeng You,*
Shie-Ming Peng, and Gene-Hsiang Lee

Three-dimensional (3D) metal-organic polymers are of intense interest because of their potential novel properties, unique microporous phases, and zeolite-like catalytic features.[1] To meet the increasing demand for large-pore structures that are suitable for catalyzing reactions of large molecules, successful synthetic strategies have been developed for preparing large, porous metal-organic frameworks.[2]

As an effective and powerful synthetic strategy, decoration and expansion of the topological networks of some inorganic dense materials have been shown to provide a new generation of highly porous metal-organic polymers.[3] Our strategy for creating such a metal-organic framework with large pores is based on expanding the zeolite topologies by construction of metal-organic tetrahedral building blocks with four connections. Such building blocks usually lead to a diamondlike topology that is often unstable owing to interpenetration of the framework through enlarged links.[4] We report here a novel 3D metal-organic framework of a tetrahedral building block, TX_4, in which the T-X-T angle is about 145°. In this structure, the TX_2 compound was prepared with a zeolite-like topology. Imidazole was chosen as a linker X since the two-coordinate N atoms of this bidentate ligand are oriented at an angle of about 144°, which is very close to the Si-O-Si angle of 145° in zeolites. For the four-connected nodes in the framework, we considered the cobalt(II) ion to be the best candidate for the T atom and that $[Co(im)_4]^{2-}$ would be a suitable building block. A different, structure-defined 3D polymer of this building block has been reported previously as a neutral framework.[5] This framework, however, has no pore opening, and furthermore, it exhibits neither the diamond topology nor the zeolite structure.

The new compound $[Co_5(im)_{10}\cdot 2MB]_\infty$ (**1**) was synthesized under solvatothermal conditions by using piperazine (PZ) as the structure-directing agent and 3-methyl-1-butanol (MB) as the solvent and space-filling agent. Though not observed in the crystalline structure, the piperazine apparently serves some structure-directing role since parallel reactions with different structure-directing agents result in different networks. Furthermore, a precipitate isolated after 12 h at room temperature prior to solvatothermal reaction, exhibits an IR spectrum with a distinctive signature for an NH stretch. The violet needle crystals of **1** were characterized by IR spectroscopy, elemental analysis, and by single-crystal X-ray structure analysis.

The X-ray structural analysis showed that the neutral 3D framework of $[Co_5(im)_{10}\cdot 2MB]_\infty$ (**1**)[6] is composed of 4-connected tetrahedral building blocks $[Co(im)_4]$. There are five T atoms in the asymmetric unit (Figure 1) and 20 T atoms in the unit cell together with eight structurally defined MB molecules. This framework exhibits a zeolitic topology, analogous to all silicate neutral frameworks, although the specific connectivity represents a topology that to the best of our knowledge has not previously been observed in molecular sieve chemistry (Figure 2). The structure of **1** contains 5- and

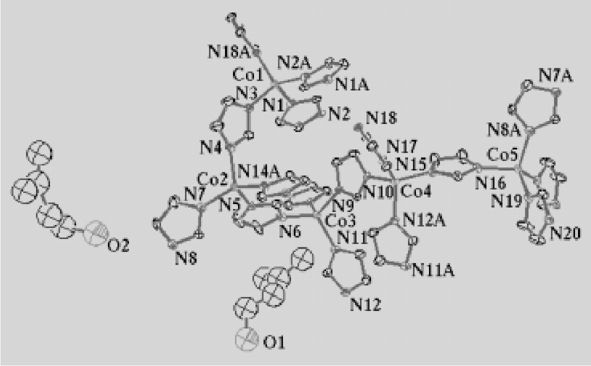


Figure 1. Coordination geometry of cobalt atoms (T atoms) in the asymmetric unit of compound **1**. Thermal ellipsoids are at 50% probability level. Selected bond lengths [Å] and angles [°] and Co···Co distances [Å]: Co1-N1 1.972(3), Co1-N3 1.983(4), Co1-N18A 1.994(4), Co1-N2A 1.990(4); N1-Co1-N3 113.0(3), N1-Co1-N18A(3) 111.6(4), N1-Co1-N2A 105.3(4), N3-Co1-N18A 108.5(5), N2-Co1-N2A 113.3(4), N18A-Co1-N2A 104.9(5); Co1···Co2 6.030(5), Co2···Co3 5.972(5), Co3···Co4 5.898(5), Co4···Co5 5.891(5).

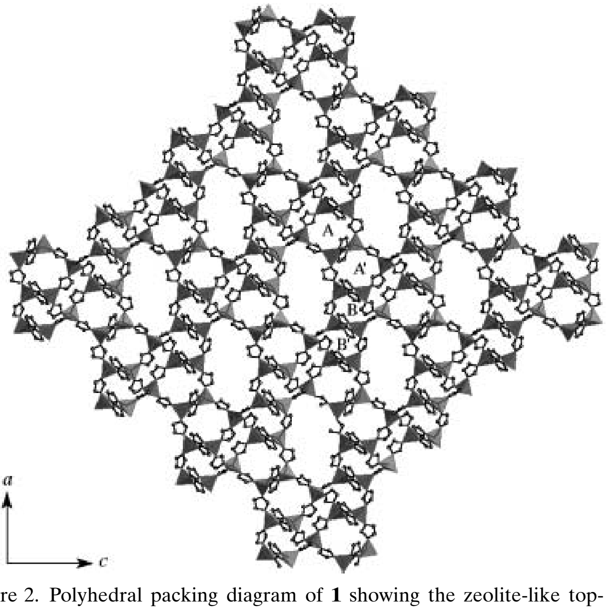


Figure 2. Polyhedral packing diagram of **1** showing the zeolite-like topology; A, A′, B, B′ are channels of the corresponding chains viewed down [010]. The hydrogen atoms and the guest MB molecules are omitted for clarity.

---

[*] Prof. X.-Z. You, Y.-Q. Tian, C.-X. Cai, Y. Ji
State Key Laboratory of Coordination Chemistry
Coordination Chemistry Institute, Nanjing University
Nanjing 210093 (PR China)
Fax: (+86) 25-3314502
E-mail: xyz@netra.nju.edu.cn

Prof. Dr. S.-M. Peng, G.-H. Lee
Department of Chemistry
National Taiwan University, Taipei (Taiwan)

[**] This work was funded by the State Key Project of Fundamental Research (No. G200077500) and the Natural Science Foundation of China. We thank Prof. Dr. Ren-Gen Xiong for production of figures. im = imidazole; MB = 3-methyl-1-butanol.

6-rings, which are made of two different chain units (chain A and chain B). These chains run along the *b* axis, and are arranged AA′BB′ along the *a* axis by using the common edges to form corrugated sheets (A′ and A, and B′ and B are related by C_2 symmetry). These sheets, which are related to each other by a center of inversion, share common vertices on the peaks of the corrugated sheets. This results in the formation of the 3D framework with sequences of parallel square rings and elliptical 8-rings. The latter forms one-dimensional (1D) channels (Figure 3), which intersect each other through offset 8-ring openings in the (110) direction and 6-ring openings in the (001) direction. The channel openings are 16.89 Å × 11.65 Å. When van der Waals radii of the atoms are taken into account, these openings are 9.42 Å × 3.87 Å. If a structure with zeolite or zeolite-like topology with 10- or even larger rings could be created by using the cobalt imidazolate, this would likely lead to materials with mesoporous phases.

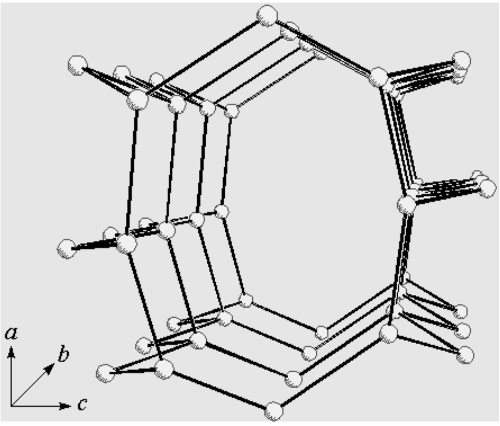


Figure 3. Ball-and-stick representation of the tubular building unit of **1**. Spheres: Co; sticks: imidazolate groups.

The MB-free compound **2** was prepared by refluxing compound **1** in ethanol for 4 h and then evacuating the product at 5×10^{-5} Torr for 6 h at room temperature. The X-ray structure of **2**[6b] shows that the MB-free compound still maintains the framework symmetry of compound **1**. However, more disordered imidazolates are observed in **2**, and ethanol molecules are found (ca. 50 % occupancy) in the chain A channels. These ethanol molecules can be then easily removed by heating the sample at 70 °C under vacuum.

Thermal gravimetric analysis (TGA) of **1** under a nitrogen stream[7] shows release of guest MB molecules between 130–220 °C leading to a weight loss of 15 %, which corresponds to the loss of all guest MB molecules. Above 220 °C, the sample shows no further weight loss up to 430 °C at which temperature the compound decomposed. The sample of fully evacuated **1** maintains its crystalline transparency, and the powder X-ray diffraction patterns are identical to that of the as-synthesized compound **1**, only with weakened intensities. However, when the above sample is soaked in MB for several hours, the intensities of the diffraction patterns recover. TGA of **2** shows release of ethanol with a weight loss of about 2 % up to 130 °C, while the framework is stable up to 430 °C. Refluxing **1** in toluene or xylene for 24 h led to a replacement of the MB molecules in **1** with toluene or xylene. The presence of toluene or xylene was detected by the new bands in the IR spectra and confirmed by the high carbon value in the elemental analyses of the corresponding samples. These solids with new guests also maintained their crystal forms and transparency. The above results reveal the robust framework of **1** and show it may endure a rather high-temperature operating condition for catalysis and separation. Therefore we consider that the cobalt imidazolate **1** is likely a real metal-organic zeotype.[8]

Experimental Section

1: $Co(Ac)_2 \cdot 4H_2O$ (2.5 mmol), imidazole (5 mmol), and piperazine (2.5 mmol) were stirred in 3-methyl-1-butanol (30 mL) at room temperature for 12 h to give a precipitate. This heterogeneous mixture was then placed in a Teflon-lined steel autoclave and heated at 140 °C for 24 h. The resulting impure dark purple single crystals of **1** are stable in air and insoluble in water and common organic solvents except organic acids such as formic and acetic acid. Further purification gave **1** in about 60 % yield. **1**: Elemental analysis (%) for $[Co_5(im)_{10} \cdot 2MB]_\infty$: calcd: C 42.08, H 4.77, N 24.54; found: C 41.81, H 4.40, N 24.38; FT-IR (KBr): $\tilde{\nu} = 3129$ (w), 3104 (w), 2956–2870 (m), 1489 (s), 1469 (s), 1084 (vs), 953 (s), 831 (m), 756 (s) 668 (s) cm^{-1}. **2**: Elemental analysis (%) for $[Co_5(im)_{10} \cdot 0.5\,EtOH]_\infty$: calcd: C 37.67, H 3.37, N 28.35; found: C 38.18, H 3.78, N 27.95; FT-IR (KBr): $\tilde{\nu} =$ 3129 (w), 3104 (w), 2955 (w), 1489 (s), 1468 (s), 1083 (vs), 952 (s), 829 (m), 754 (s) 667 (s) cm^{-1}.

Received: August 29, 2001
Revised: December 10, 2001 [Z17819]

---

[1] a) P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem.* **1999**, *111*, 2798–2848; *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684; b) A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466–3492; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268–3292; c) D. Gatteschi, *Adv. Mater.* **1994**, *6*, 635.

[2] a) M. J. Zaworotko, *Nature* **1999**, *402*, 242–243; b) H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279.

[3] a) 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; b) M. O'Keeffe, M. Eddaoudi, H. Li, T. M. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3–20; c) B. Chen, M. Eddaoudi, S. T. Hyde, M. O'Keeffe, O. M. Yaghi, *Science* **2001**, *291*, 1021–1023.

[4] a) S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494; b) B. F. Hoskins, R. Roberson, *J. Am. Chem. Soc.* **1990**, *112*, 1546–1554.

[5] a) M. Sturm, F. Bromdl, D. Engel, W. Hoppe, *Acta Crystallogr. Sect. B* **1975**, *31*, 2369–2378; b) F. Seels, J. Rodrian, *J. Organomet. Chem.* **1969**, *16*, 479–484.

[6] a) A violet crystal of $[Co_5(im)_{10} \cdot 2MB]_\infty$ (**1**) was selected for X-ray structural analysis on a Bruker SMART CCD diffractometer at 150(1) K. The compound crystallized in the space group $P2_1/n$, monoclinic, dimensions $0.37 \times 0.10 \times 0.07$ mm, $a = 24.3406(8)$, $b = 9.4526(3)$, $c = 24.8470(8)$ Å, $\beta = 91.877(1)^\circ$, $V = 5713.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.327$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 1.470$ mm^{-1}, $F(000) = 2340$. A total of 43 981 reflections were collected in the range of $1.15^\circ \leq \theta \leq 26.40^\circ$, of which 11 707 were unique reflections and 6306 with $I \geq 2\sigma(I)$ were collected for the analysis. The structure was solved and refined by full-matrix least-squares on F^2 values (SHELXL-97). Non-hydrogen atoms (excluding those of solvent molecules) were refined anisotropically, of which C10, C11 (C10′, C11′) are disordered and were modeled in 70 % (30 %) SOF. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. The final indices were $R1 = 0.0688$, $Rw2 = 0.230$ with goodness-of-fit = 1.027. b) A violet crystal of $[Co_5(im)_{10} \cdot 0.5\,EtOH]_\infty$ (**2**) was selected for X-ray structure analysis on a Bruker SMART CCD diffractometer at

293(2) K. The compound crystallized in the space group $P2_1/n$, monoclinic, dimensions $0.35 \times 0.10 \times 0.08$ mm, $a = 24.246(5)$, $b = 9.5182(19)$, $c = 24.685(8)$ Å, $\alpha = 90.96(3)^\circ$, $V = 5696(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.153$ Mg m^{-3}, $\lambda = 0.71073$ Å, $\mu(\mathrm{Mo_{K\alpha}}) = 1.463$ mm^{-1}, $F(000) = 1992$. A total of 34441 reflections were collected in the range of $1.65^\circ \leq \theta \leq 28.02^\circ$, of which 13040 were unique reflections and 4517 with $I \geq 2\sigma(I)$ were collected for the analysis. The structure was solved by full-matrix least-squares on F^2 values (SHELX-97). Non-hydrogen atoms (excluding disordered and solvent atoms) were refined anisotropically. The disordered atoms were modeled in 50 % SOF. Hydrogen atoms were fixed at calculated positions and refined by using a riding mode. The final indices were $R1 = 0.0561$, $Rw2 = 0.1149$ with goodness-of-fit = 1.023. CCDC-168798 (**1**) and CCDC-168799 (**2**) 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).

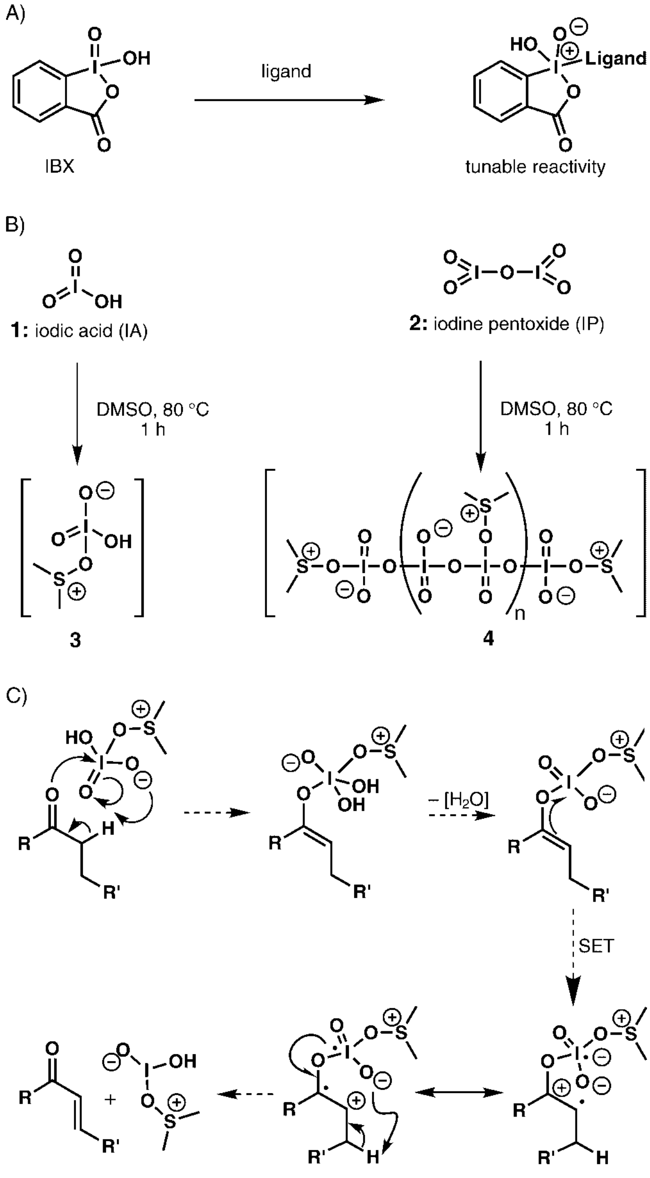
[7] Thermal analyses were carried out using a TA-SDT 2960 apparatus at a heating rate of 5 K min^{-1} from 20 to 1000 °C under a flux of nitrogen: 6.8505 mg of the sample **1** and 11.9348 mg **2** were used for the measurement.

[8] D. M. L. Goodgame, D. A. Grachvogel, D. J. Williams, *Angew. Chem.* **1999**, *111*, 1217–219; *Angew. Chem. Int. Ed.* **1999**, *38*, 153–156.

HIO_3 and I_2O_5: Mild and Selective Alternative Reagents to IBX for the Dehydrogenation of Aldehydes and Ketones[**]

K. C. Nicolaou,[*] Tamsyn Montagnon, and Phil S. Baran

Although the chemistry of iodine(III) and iodine(VII) reagents has been extensively explored,[1] that of the iodine(V) manifold, which includes reagents such as 1-hydroxy-1,2-benziodoxal-3(1H)-one-1-oxide (IBX) and Dess–Martin periodinane (DMP), remained until recently almost entirely relegated to being a source of reliable agents for the simple oxidation of alcohols and for a number of closely related processes.[2] However, a recent discovery that stems from endeavors in total synthesis in our laboratories[3] has opened the door to the development of a number of novel iodine(V)-mediated reactions.[4–11] Furthermore, detailed mechanistic studies into one of these processes, the IBX-mediated dehydrogenation of ketones and aldehydes,[10, 11] led to the recognition of the importance of the ligand appended to the iodine nucleus in this and other SET-based process (Scheme 1 A).[7] Armed with this information, we were able to tune the reactivity at the iodine nucleus by using a variety of *N*-oxide ligands, and hence developed a mild room-temperature variant of the original IBX dehydrogenation with expanded functional group tolerance.[12] With such dramatic changes in reactivity patterns on changing the ligand from THF[7, 8] or DMSO[10, 11] to an *N*-oxide,[12, 13] we began to question the role of all the substituents on the iodine nucleus, including the aromatic core. Herein we report initial results that probe the latter question and provide us with a number of economic, commercially available, and safe iodine(V) dehydrogenation agents whose structures contain no aromatic moiety.



Scheme 1. A) The tunable reactivity of IBX by using different ligands prompted the investigation of the role of the aromatic moiety. B) This led to development of **3** and **4** as dehydrogenating agents. C) Postulated mechanism of action.

---

[*] Prof. Dr. K. C. Nicolaou, Dr. T. Montagnon, Dr. P. S. Baran
Department of Chemistry and The Skaggs Institute for Chemical Biology
The Scripps Research Institute
10550 North Torrey Pines Road, La Jolla, California 92037 (USA)
Fax: (+1) 858-784-2469
E-mail: kcn@scripps.edu

and
Department of Chemistry and Biochemistry
University of California San Diego
9500 Gilman Drive, La Jolla, California 92093 (USA)

[**] We thank Dr. D. H. Huang, Dr. G. Suizdak, and Dr. Raj Chahda for NMR spectroscopic, mass spectrometric, and X-ray crystallographic assistance, respectively. Financial support for this work was provided by The Skaggs Institute for Chemical Biology, fellowships from GlaxoWellcome (T.M.) and the National Science Foundation (P.S.B.), and grants from Amgen, Array Biopharma, Boehringer-Ingelheim, Glaxo, Hoffmann-LaRoche, DuPont, Merck, Novartis, Pfizer, and Schering Plough.