Supplementary Data

Water Nanotubes Clathrating Solvent Molecules Stabilized by Molecular 1-D Nanoporous Crystal

Makoto Tadokoro, * Chihiro Iida, Yuriko Shimazaki, Kyosuke Isoda, You Suzuki, Tomoaki Sugaya, Yoshihide Kumagai, and Motohiro Mizuno

Experimetals

Fig. S1  WNT structure at 90 K with O(4B), O(5B), O(11B)
Fig. S2  WNT structure at 90 K with O(4A), O(5A), O(11A)
Fig. S3  Perspective view along the $a$ axis
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Fig. S12 WNT structures at 253 K and 90 K
Fig. S13 TG and TG-mass images of crystal 3
Fig. S14 Five polyhedral of three natural clathrate hydrates
Preparation of crystal 3: The H2O: THF = 4/1 (v/v) solution with dissolved [RuIII(H2bim)3](NO3)3 (0.026 g 0.04 mmol) was mixed with a weak alkaline water solution of Cs3TMA (0.01 g 0.04 mmol). After two weeks, the blue hexagonal crystal 3 was obtained (yield 53.4%). IR (KBr) (cm–1): 3417, 3126, 2775, 2306, 1704, 1612, 1558, 1428, 1361, 1263, 1002, 929, 757 . Anal. calcd. elemental analysis for [Ru(H2bim)3](TMA)· 5.25H2O· 0.25THF (C28H33.5N12O11.25Ru) (dried for 4 h at 100 ˚C in vacuo): C, 40.61%; H, 3.87%; N, 20.17%; found: C, 40.85%; H, 4.10%; N, 20.42%. TG spectrum of 3: weight loss 34.80% (240 ˚C); 34.74% calculated for (H2O)30·(THF)3/{[Ru(H2bim)3](TMA)}2·(H2O)30·(THF)3. 2H-NMR: Solid-state 2H NMR spectra were measured using a Chemagnetics CMX-300 spectrometer operated at 45.826 MHz with a quadrupole echo pulse sequence. The spin-lattice relaxation times (T1) were measured using the inversion recovery method.

Crystal data for crystal 3 at 253 K: Crystal dimensions: 0.32 × 0.16 × 0.15 mm³. C₃₃H₆₃N₁₂O₂₂.5Ru, M = 1089.02, orthorhombic, space group Fddd (#70), a = 10.7966(13) Å, b = 31.961(4) Å, c = 59.200(7) Å, V = 20428(4) Å³, Z = 16, F(000) = 9104, Dcalc = 1.416 g cm⁻³, µ(Mo Kα) = 3.94 cm⁻¹, T = 253 K, radiation = 0.71073 Å, R₁ = 0.0595 for I > 2.0σ(I), wR2 = 0.1849 for all data (5844 reflections), GOF = 1.262 (283 parameters). The maximum and minimum highest peaks in the final differential map are 0.820 and –0.655 e/Å³, respectively.

Crystal data for crystal 3 at 104 K: Crystal dimensions are the same as at 253 K. C₃₃H₆₃N₁₂O₂₂.5Ru, M = 1089.02, orthorhombic, space group Fddd (#70), a = 10.7503(10) Å, b = 32.010(3) Å, c = 59.140(6) Å, V = 20351(3) Å³, Z = 16, F(000) = 9104, Dcalc = 1.422 g cm⁻³, µ(Mo Kα) = 3.95 cm⁻¹, T = 90 K, radiation = 0.71073 Å, R₁ = 0.0820 for I > 2.0σ(I), wR2 = 0.2387 for all data (5804 reflections), GOF = 1.554 (307 parameters). The maximum and minimum highest peaks in the final differential map are 1.917 and –0.990 e/Å³, respectively. The single crystal of 3 was mounted at 253 K and 90 K using a loop method. Diffraction data were measured on a Bruker APEX CCD-detector X-ray diffractometer with monochromatized Mo Kα radiation from a rotating anode source apparatus. Data reduction, structure solution and refinement, and all the necessary computational data processes were carried out using the APEX, SAINT, and SHELXTL programs. The positions of the three THF molecules contained in crystal 3 could not be determined because of heavy disordering. Therefore, the average electron densities of the THF molecules were calculated as O(12) sites by X-ray structure analysis. Crystallographic data, excluding the structure data, have been deposited with the Cambridge Crystallographic Data Centre (CCDC), in the form of supplementary publication numbers CCDC 732770 for crystal 3 at 253 K and CCDC 732771 for crystal 3 at 90 K. A copy of the data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK [Direct Line: +44 1223 762910, Fax: +44 (0) 1223-336033, or e-mail: deposit@ccdc.cam.ac.uk].
WNT periodic unit structure at 90 K contained the disordered O(4A), O(5A), and O(11A): The red lines show H-bonding networks between H₂O molecules of the red spheres and indicate H-bonding lengths with the range of less than 3.9 Å.
WNT periodic unit structure at 90 K contained the disordered O(4B), O(5B), and O(11B): The light-blue lines show H-bonding networks between H₂O molecules of the light-blue spheres and indicate H-bonding lengths with the range of less than 3.6 Å.
Figure S3

Perspective view along the $a$ axis for the 3-D nanoporous framework formed from $[\text{Ru(H}_2\text{bim)}_3]^{3+}$ and TMA$^{3-}$ building blocks. The light-blue networks are represented a H-bonding $6^1$ spiral and the red ones are a $6^6$ spiral. The blue spheres are represented Ru$^{3+}$ ions.
Figure S4

Perspective view along the c axis for the 3-D nanoporous framework formed from [Ru(H₂bim)₃]³⁺ and TMA³⁻ building blocks. The light-blue networks are represented a H-bonding 6¹ spiral and the red ones are a 6⁵ spiral. The blue spheres are represented Ru³⁺ ions.
Figure S5

Perspective view along the $b$ axis for the 3-D nanoporous framework formed from $[\text{Ru(H}_2\text{bim)}_3]^{3+}$ and TMA$^{3-}$ building blocks. The light-blue networks are represented a H-bonding $6^1$ spiral and the red ones are a $6^5$ spiral. The blue spheres are represented Ru$^{3+}$ ions.
Figure S6

Perspective view along the 1-D nanochannels in crystal structure at 90 K of
{[Ru(H$_2$Bim)$_3$]$_2$(TMA)$_2$·30H$_2$O·3THF)$_n$ (3): The red lines show H-bonding networks of
WNT and The light-blue spheres show the nanoporous frameworks.
Figure S7

Perspective view along the 1-D nanochannels in crystal structure at 254 K of \( ([\text{Ru(H}_2\text{bim})_3]_2(\text{TMA})_2\cdot3\text{H}_2\text{O}\cdot3\text{THF})_n \) (3): The red lines show H-bonding networks of WNT and the light-blue spheres show the nanoporous frameworks.
Comparison with DSC Measurements on Melting Points of \([\text{Ru(H}_2\text{bim})_3]\text{(TMA)}\) Porous Molecular Crystals with Containing WNT of Novel Clathrate Hydrate Clusters Clathrated 1,4-dioxane, EtOH, \(\text{Me}_2\text{CO}\), THF
Temperature-dependent solid-state $^2$H-NMR spectra for a long relaxation time $T_{1L}$ of $\{[\text{Ru(H}_2\text{bim)}_3]\text{TMA}_2\cdot\text{30H}_2\text{O}\cdot\text{3(d}^8\text{-THF})\}_n$ (9')
Temperature-dependent solid-state $^2$H-NMR spectra for a short relaxation time $T_{1S}$ of $\{[\text{Ru(H}_2\text{bim)}_2\text{TM}_2\text{O}_3\text{H}_2\text{O}_3\text{THF})]_n \}$.
Plots of spin-lattice relaxation times of $^2$H-NMR spectra for crystal 3 as a function of inverse temperature. The opened blue squares represent relaxation times for $T_{1L}$ of bulk d$^8$-THF hydrate constructed from d$^8$-THF and H$_2$O in addition to the stabilizing crystals. The opened red circles represent relaxation times for $T_{1S}$ of d$^8$-THF included in the WNT in crystal 3. The blue and red lines are represented the result of fitting for the relaxation times by Cole-Davidson distribution. ($T_{1L}$: $e^2Qq/h = 107$ kHz, $\tau_0 = 6.8\times10^{-13}$ s, $E_{ad} = 3.4$ kJ/mol, $\beta = 0.33$) ($T_{1S}$: $e^2Qq/h = 121$ kHz, $\tau_0 = 6.8\times10^{-18}$ s, $E_{ad} = 39$ kJ/mol, $\beta = 0.25$, and $\tau_0 = 0.67$ sec$^{-1}$, $E_{at} = 4.4$ kJ/mol)
1-D WNT structures included into nano-channels of \{[\text{Ru}(\text{H}_2\text{bim})_2]\text{(TMA)}_2 \cdot 30\text{H}_2\text{O} \cdot 3\text{THF}\} (3): WNT structure at 254 K (a) and 90 K (b) are represented. The red spheres and lines show H\text{2}O molecules belonging to the primary hydrate layer and the H-bonds, respectively. The light-blue spheres and lines show those belonging to a secondary hydrate layer.
Figure S13

(a): TG image of 3, 30 THF is calculated by X-ray crystal structure. (b) TG-mass image: The red lines show the disassembling fragment peak of 3 by El-mass at 354 K. The blue lines show the reference of the disassembling fragment peak of THF.
Figure 14S

Five polyhedral water clusters that form the three natural clathrate hydrates