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Simplified bicyclic cage-type molecule as a C_3-symmetric host: X-ray and FTIR characterization of encapsulation of a nitrile molecule

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Abstract We synthesized a new amine-type host molecule **2** by 2 steps, using 1,3,5-tris(aminomethyl)-2,4,6-trimethyl-benzene and 2,6-pyridinedicarboxaldehyde as starting materials. Recrystallization of **2**·6H$_2$O from hot acetonitrile, hot propionitrile and hexane/benzonitrile solutions gave colorless crystals of MeCN@**2**·MeCN·2H$_2$O, EtCN@**2**·EtCN, and 8H$_2$O@**2**·PhCN. In the former two crystals, the nitrile compounds were captured inside of the cavity of **2**. On the other hand, in the latter one, the benzonitrile was laid outside **2**. Infrared spectral measurements of MeCN@**2**·MeCN·2H$_2$O, EtCN@**2**·EtCN, and 8H$_2$O@**2**·PhCN showed that absorption bands assignable to the C $\equiv$ N stretching vibrations of nitrile compounds were observed at 2240, 2241, and 2226 cm^{-1} for MeCN@**2**·MeCN·2H$_2$O, EtCN@**2**·EtCN, and 8H$_2$O@**2**· PhCN, respectively. The former two peaks shifted to a lower energy region by 6–13 and 21–26 cm^{-1} than those of liquid and gas phases of MeCN and EtCN, respectively. That for 8H$_2$O@**2**·PhCN shifted to a slightly lower region by 2 and 12 cm^{-1} those of liquid and gas states of PhCN, respectively, indicating that the outer benzonitrile molecule dose not so much interact with **2** in the crystal.

Introduction

It has been reported that many kinds of host materials encapsulate guest molecules inside of their cavities [1]. In a few decades, cryptophanes [2, 3], multi-bridged calixarenes [4, 5], and self-assembled resorcinarene capsules [6–9] have been reported to play a role as a cage and capsule type host material. Recently, many kinds of cage-type compounds have been constructed with metal-coordination frameworks [10–15]. Although various types of synthetic host compounds can recognize and include a large number of guest molecules, we focus on the simplified molecular systems for practical and convenient uses.

Anslyn et al. synthesized a bicyclic cyclophane bridged with three 2,6-diamidepyridines, the amide-type cage compound (**I**) (Fig. 1a), which recognized several neutral and anionic molecules, as a host molecule [16, 17]. In the structures, hydrogen bonding networks were formed between the amide NH groups and H-acceptor sites of the guest molecules [16, 17]. Among many guest molecules, we focused on a neutral guest molecule of nitrile compounds. Because many amide compounds have been produced from the corresponding nitrile compounds by chemical industries, so their activation and hydrolysis are important subjects for the production of amide compounds from their nitrile materials and for the solution of environmental pollution problems with nitrile compounds.

Here, we report a new synthetic procedure for facile preparation of an amine-type bicyclic analogue of **I** and its encapsulation properties of nitrile guest molecules.

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Fig. 1 Structure of (**a**) **I** and (**b**) a new amine-type host molecule **2**
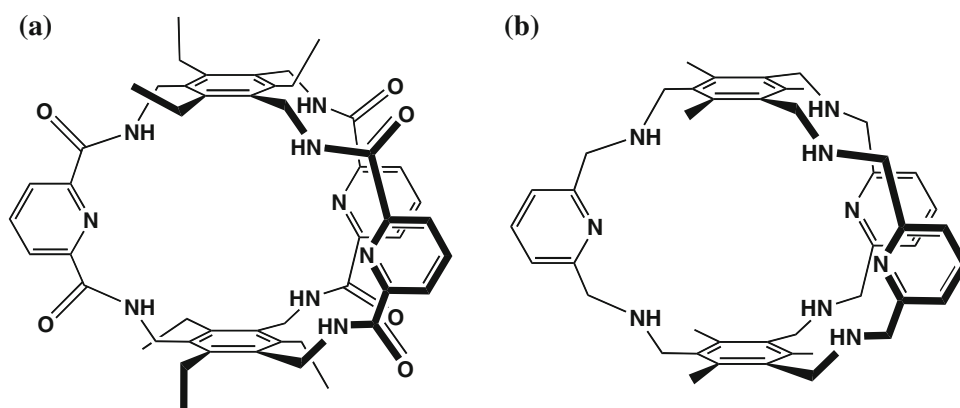
Experimental

General information

All the chemicals used were of the highest grade available and were further purified before use [18]. Elemental analysis was performed using a Perkin Elmer 2400II CHNS/O analyzer. ^{1}H-NMR spectra were measured on a Gemini 300 MHz NMR spectrometer and the chemical shift values were referenced to TMS as an internal standard. Samples of FTIR study were prepared as KBr pellets and measured by using a Jasco FTIR-4200 spectrophotometer. ESI-Mass spectra were recorded on a Micromass LCT spectrometer.

Synthetic procedures for cage-type hosts, **1** and **2** [19]

Syntheses of imine-type host **1** and amine-type host **2**·6H$_2$O

A methanol solution (200 mL) of 2,6-pyridinedicarboxaldehyde (2.50 g, 18.5 mmol) was dropped to a methanol solution (200 mL) of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene [16, 17, 20] (2.47 g, 12.3 mmol) for 2 h at room temperature. A white solid product of **1**[1] was precipitated and filtered out (Yield: 4.07 g, ca. 90%). An ethanol solution (300 mL) of NaBH$_4$ (2.25 g, 59.5 mmol) was dropped to a dichloromethane solution (300 mL) of the imine-type host **1** and the solution was stirred at room temperature for 30 h. The reaction mixture was acidified with 0.1 N HClaq and alkalified with 1 N KOHaq. The reaction mixture was evaporated under reduced pressure, and the white precipitate was separated by filtration. The filtrate was extracted with 100 mL ethylacetate in three times. The

collected organic layer was dried with anhydrous MgSO$_4$, and the solvent was removed by evaporation, giving white residual products. Recrystallization of these crude products from a hot methanol solution at 40 °C gave pure amine-type host **2**·6H$_2$O (Yield: 2.37 g, 48%) as colorless crystalline precipitate. ^{1}H-NMR (CDCl$_3$, 300 MHz) 7.52 (dd, 3H, $J = J' = 7.8$ Hz, Py-H), 7.03 (d, 6H, $J = 7.8$ Hz, Py-H), 3.97 (s, 12H, CH$_2$), 3.80 (s, 12H, CH$_2$), 2.32 (s, 18H, CH$_3$) ppm. FTIR (cm^{-1}, KBr): 3394, 3272, 2916, 2850, 1592, 1577, 1450, 1093, 1066. Elemental analysis: calcd. (%) for C$_{45}$H$_{57}$N$_9$·6H$_2$O (C$_{45}$H$_{69}$N$_9$O$_6$): C: 64.95; H: 8.36; N: 15.15. Found: C: 64.85; H: 8.43; N: 14.98.

Synthetic procedures for host **2** including various kinds of guest molecules

Synthesis of MeCN@**2**

The amine-type host **2**·6H$_2$O (7.0 mg, 8 µmol) was added to 1 mL acetonitrile. After heating and dissolving the suspended solution at 60 °C, 0.1 mL methanol was added. The solution was allowed to stand for 2 days at room temperature, giving MeCN@**2**·MeCN·2H$_2$O (Yield: 3.0 mg, 39%) as colorless crystals. Elemental analysis: calcd. (%) for C$_{45}$H$_{57}$N$_9$·CH$_3$CN·6 H$_2$O (C$_{47}$H$_{72}$N$_{10}$O$_6$): C: 64.65; H: 8.31; N: 16.04. Found: C: 64.52; H: 7.95; N: 15.93. ESI-Mass: m/z 724.5 (M + H$^+$). ^{1}H-NMR (CDCl3, 300 MHz) 7.52 (dd, 3H, $J = J' = 7.8$ Hz, Py-H), 7.03 (d, 6H, $J = 7.8$ Hz, Py-H), 3.95 (s, 12H, CH$_2$), 3.79 (s, 12H, CH$_2$), 2.30 (s, 18H, CH$_3$), 2.00(s, 6H, CH$_3$) ppm.

Synthesis of EtCN@**2**

The amine-type host **2**·6H$_2$O (7.0 mg, 8 µmol) was added to 1 mL propionitrile. After heating and dissolving the suspended solution at 70 °C. The solution was allowed to stand for one day at room temperature, giving EtCN@**2**·EtCN (Yield: 1.0 mg, 14%) as colorless crystals. Elemental analysis: calcd. (%) for C$_{45}$H$_{57}$N$_9$·2 CH$_3$CH$_2$CN (C$_{51}$H$_{67}$N$_{11}$): C: 73.43; H: 8.10; N: 18.47. Found: C: 73.25;

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[1] Data for imine-type host **1**: Recrystallization from CH$_2$Cl$_2$/Et$_2$O. ^{1}H-NMR (CDCl$_3$, 300 MHz) 8.16 (d, 6H, $J = 7.8$ Hz, Py-H), 8.00 (s, 6H, CH = N), 7.78 (dd, 3H, $J = J' = 7.8$ Hz, Py-H), 5.12 (s, 12H, CH$_2$), 2.11 (s, 18H, CH$_3$) ppm. FTIR (cm^{-1}, KBr): 2925, 2881, 1645, 1586, 1571, 1456, 1437, 963, 811. Elemental analysis: calcd. (%) for C$_{45}$H$_{45}$N$_9$·0.5 CH$_2$Cl$_2$ (C$_{45.5}$H$_{46}$N$_9$Cl): C: 72.44; H: 6.15; N: 16.71. Found: C: 72.65; H: 6.20; N: 16.80

H: 8.29; N: 18.32. ESI-Mass: m/z 724.4 (M + H$^+$), 746.3 (M + Na$^+$). ^{1}H-NMR (CDCl$_3$, 300 MHz) 7.51 (dd, 3H, $J = J' = 7.8$ Hz, Py-H), 7.04 (d, 6H, $J = 7.8$ Hz, Py-H), 3.87 (s, 12H, CH$_2$), 3.80 (s, 12H, CH$_2$), 2.37 (q, 4H, $J = 7.5$ Hz, CH$_2$), 2.24 (s, 18H, CH$_3$), 1.30 (t, 6H, $J = 7.5$ Hz, CH$_3$) ppm.

Synthesis of 2·PhCN

The amine-type host **2**·6H$_2$O (7.0 mg, 8 μmol) was dissolved to 0.5 mL benzonitrile. Large excess amount of *n*-hexane (ca. 5 mL) was added to the solution, and it was allowed to stand for a few days at room temperature, giving 8H$_2$O@**2**·PhCN (Yield: 6.0 mg, 73%) as colorless crystals. Elemental analysis: calcd. (%) for C$_{45}$H$_{57}$N$_9$·C$_6$H$_5$CN·8 H$_2$O (C$_{52}$H$_{78}$N$_{10}$O$_8$): C: 64.31; H: 8.09; N: 14.42. Found: C: 64.51; H: 7.96; N: 14.50. ESI-Mass: m/z 724.5 (M + H$^+$), 746.4(M + Na$^+$). ^{1}H-NMR (CDCl$_3$, 300 MHz) 7.48–7.68 (m, 5H, Ar–H),7.52 (dd, 3H, $J = J' = 7.8$ Hz, Py-H), 7.03 (d, 6H, $J = 7.8$ Hz, Py-H), 3.93 (s, 12H, CH$_2$), 3.79 (s, 12H, CH$_2$), 2.29 (s, 18H, CH$_3$) ppm.

X-ray Crystallography of MeCN@**2**·MeCN·2H$_2$O, EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN ^{2}

The well-shaped single crystals of MeCN@MeCN·2H$_2$O, EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN suitable for X-ray diffraction measurements were obtained from the corresponding solution by allowing the solution to stand for a few days at room temperature as described above. The crystals were mounted on a glass fiber, and the diffraction data were collected on RIGAKU/MSC Mercury CCD using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at −100 °C. In order to determine the cell constants and orientation matrices, twelve oscillation photographs were taken for each frame with the oscillation angle of 3° and the exposure time of 10, 10 and 15 s. for MeCN@**2**·MeCN· 2H$_2$O, EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN, respectively. Reflection data were collected for both Lorentz and polarization effects. The structures of EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN were solved by the direct method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Each refinement was continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic

^{2} Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.CCDC 739562 and 739563 for EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN. These data can be obtained free of charge via http://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 e-mail: deposit@ccdc.cam.ac.uk

Table 1 Crystallographic data for EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN

	EtCN@**2**·EtCN	8H$_2$O@**2**·PhCN
Formula	C$_{51}$H$_{67}$N$_{11}$	C$_{52}$H$_{78}$N$_{10}$O$_8$
Formula weight	834.16	971.25
Crystal color, habit	Colorless, prism	Colorless, prism
Crystal dimensions (mm)	0.40 × 0.35 × 0.20	0.40 × 0.40 × 0.25
Crystal system	Triclinic	Triclinic
a (Å)	12.7474(5)	12.4615(19)
b (Å)	13.0331(6)	13.931(2)
c (Å)	15.4937(8)	16.053(3)
α (°)	109.397(2)	94.0971(17)
β (°)	92.5810(19)	105.938(2)
γ (°)	100.6720(11)	93.5602(18)
V (Å^3)	2370.18(19)	2663.1(7)
Space group	P$\bar{1}$	P$\bar{1}$
Z value	2	2
D (g/cm^3)	1.169	1.211
$F(000)$	900.00	1048.00
μ (Mo Kα)/cm^{-1}	0.712	0.827
$2\theta_{max}$/°	55.0	55.0
Observed reflections	19049	21495
Independent reflections	10428	11727
Reflection/parameter ratio	18.62	18.53
No. of variables	560	633
$R1$ [$I > 2\sigma(I)$]^a	0.0493	0.0564
R_w (all data)^b	0.1589	0.1850

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$ data. ^{b} $R_w = [\Sigma(\omega(F_o^2 - F_c^2)^2)/\Sigma\omega(F_o^2)^2]^{1/2}$; $\omega = 1/[\sigma^2(F_o^2) + (0.1000 \cdot P)^2 + 0.0000 \cdot P]$ for EtCN@**2**·EtCN, $\omega = 1/[\sigma^2(F_o^2) + (0.1189 \cdot P)^2 + 0.9127 \cdot P]$ for 8H$_2$O@**2**·PhCN, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$

scattering factors and anomalous dispersion terms were taken from the literature [21]. Hydrogen atoms were located at the calculated positions and were assigned as a fixed displacement, where the thermal parameters of calculated hydrogen atoms were related to those of their parent atoms by $U(H) = 1.2U_{eq}(C, N)$. All the calculations were performed by using the Crystal Structure (Ver. 3.8) program package [22]. Summaries of the fundamental crystal data and experimental parameters for structure determination are given in Table 1 for EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN. Those of MeCN@**2**·MeCN·2H$_2$O are described in footnote 3.

Results and discussion

In this paper, we report a new bicyclic cage-type compound, **2**, bridged by three 2,6-di(aminomethyl)pyridine (Fig. 1b). As shown in Scheme 1, we initially synthesized imine-type **1**

Scheme 1 Synthesis of a new amine-type host molecule, **1** and **2**
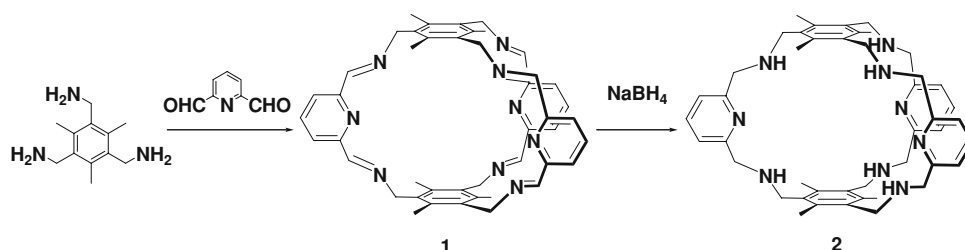
from 3 equiv. of 2,6-pyridinedicarboxaldehyde and 2 equiv. of 1,3,5-tris(aminomethyl)-2,4,6-trimethylbenzene [16, 17, 20] by self-assembly of these components upon formation of Shiff-base C = N bonds. The latter material was prepared by catalytic hydrogenation of an azide-substituted compound for bromide groups in 1,3,5-tris(bromomethyl)-2,4,6-trim-ethylbenzene. The amine-type host molecule **2** was prepared by hydrogenation of the imine-type host **1** with 10.4 equiv. of sodium borohydride. Host molecules **1** and **2** were confirmed by elemental analytical and ^{1}H-NMR and FTIR spectro-scopic methods.

The pure bicyclic cage compound **2** was obtained as a 6-hydrated compound, **2**·6H$_2$O, by recrystallization from its methanol solution. In case of recrystallization in acetonitrile/methanol solution, **2** was isolated as a crystal containing acetonitrile. The preliminary result of X-ray analysis for this crystal showed that the cage compound **2** captured one acetonitrile molecule inside **2** (MeCN@**2**), as shown in Fig. 2, without catching methanol molecules, although unfortunately we could not succeed in fully refining the crystal structure of MeCN@**2**·MeCN·2H$_2$O[3]. It has been previously reported that the amide-type cage compound (**I**) captures one acetnitrile molecule [16] in the mode similar to that of **2**. In order to understand details of interaction modes between the cage-type compound **2** and nitrile molecules, we carried out recrystallization of **2**·6H$_2$O in other nitrile sol-vents to obtain suitable crystals for X-ray analysis.

In propionitrile solution of **2**, we succeeded in obtaining good crystals suitable for X-ray diffraction experiment. The X-ray diffraction analysis revealed that two propioni-trile molecules were contained in the unit cell. One pro-pionitrile molecule was encapsulated inside the cavity of the host molecule **2** in the mode similar to those of MeCN@**2** (Fig. 2) and amide-type host **I** reported previ-ously [16], and another propionitrile molecule was laid close to those of two bridging di(aminomethyl)pyridine
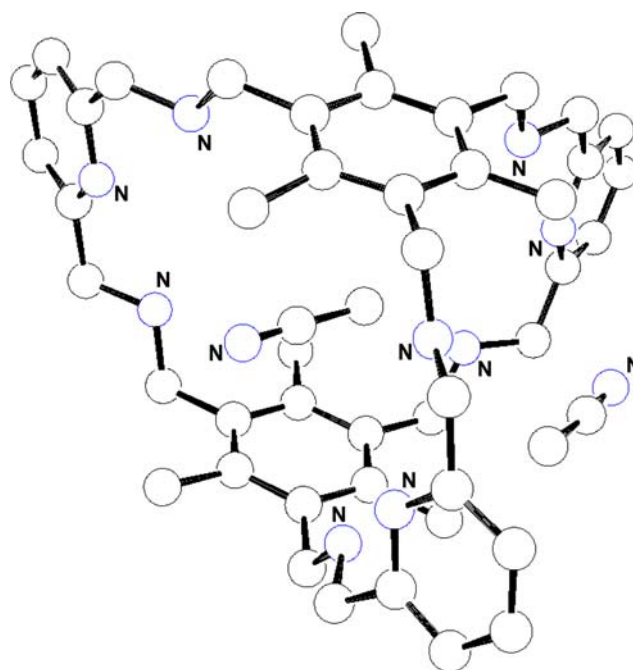

Fig. 2 The structure view of MeCN@**2**·MeCN·2H$_2$O. All hydrogen atoms and disordered oxygen atoms were omitted for clarity
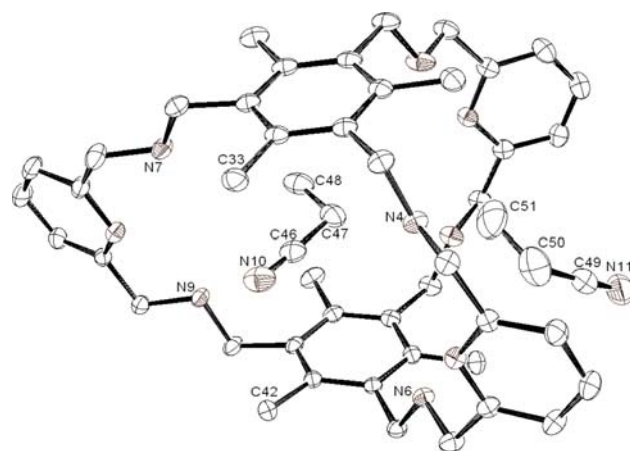

Fig. 3 ORTEP view of EtCN@**2**·EtCN drawn with the thermal ellipsoids at the 30% probability level and atomic labeling scheme. All hydrogen atoms were omitted for clarity

units of **2**. (EtCN@**2**·EtCN), as shown in Fig. 3. The selected bond lengths and angles of EtCN@**2**·EtCN are listed in Table 2. In the crystal structure of EtCN@**2**·EtCN,

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[3] Crystallographic data for MeCN@**2**·MeCN·2H$_2$O: Formula; C$_{49}$H$_{63}$N$_{11}$O$_2$, Formula Weight; 838.11, Crystal Color, Habit; color-less, prism, Crystal Dimensions (mm); 0.50 × 0.30 × 0.25, Crystal System; monoclinic, a (Å); 14.858(5), b (Å); 17.085(6), c (Å); 19.150(7), β (°); 102.075(4), V (Å^3); 4754(3), Space Group; P2$_1$/n, Z value; 4, D (g/cm^3); 1.171, $F(000)$; 1800.00, μ(Mo Kα)/cm^{-1}; 0.743, $2\theta_{max}$/°; 55.0, Observed reflections; 37206, Independent reflections; 10900, Reflection/Parameter ratio; 16.82, No. of Variables; 648, $R1$[I > 2σ(I)]; 0.1246, R_w (all data); 0.2850

Table 2 Selected bond lengths (Å) and angles (°), and selcted atomic distances (Å) for EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN

	EtCN@**2**·EtCN	8H$_2$O@**2**·PhCN
Bond length (Å)		
C–N	C46-N10 1.142 (2)	C46-N10 1.142 (3)
	C49-N11 1.138 (3)	
C–CN	C47-C46 1.461 (2)	C47-C46 1.443 (3)
	C50-C49 1.469 (4)	
Bond angle (°)		
C–C–N	C47-C46-N10 178.6 (2)	C47-C46-N10 179.7 (2)
	C50-C49-N11 176.3 (2)	
Atomic distances (Å)		
N$_{nitrile}$···N$_{amine}$	N10···N7 3.544	–
	N10···N9 3.928	
	N10···N4 4.439	
	N10···N6 4.359	
C$_{nitirile}$···N$_{amine}$	C46···N7 3.618	–
	C46···N9 3.830	
	C46···N4 4.342	
	C46···N6 4.272	

C ≡ N and C–CN bond lengths of these inner and outer propionitrile molecules are ca. 1.14 Å and 1.46–1.47 Å, as shown in Table 2. These bond lengths agree well with those of triple and single bonds, respectively, exhibiting no significant difference between inner and outer propionitrile molecules. Both the C ≡ C–N angle values of these propionitrile molecules (176–179°) are almost 180°. Interestingly, this inner propionitrile molecule was catched between two benzene rings of **2** and the C ≡ N group, C46–N10, was located at the center of four secondary amino nitrogen atoms, N4, N6, N7, and N9, belonging to the two di(aminomethyl)pyridine units in **2**. The nitrogen atom, N10, of the included propionitrile molecule did not efficiently interact with two secondary NH group by hydrogen bonding, the intermolecular distances between non-hydrogen atoms being N10···N7 = 3.62 Å and N10···N9 = 3.83 Å (Table 2). In the crystal structure of previous reported amide-type host **I**, the corresponding intermolecular distances were N$_{ntrile}$···NH$_{amide}$ = 3.28 and 3.32 Å [16]. The other intermolecular distances between the encapsulated propionitrile and secondary NH groups of **2** were N10···N4 = 4.44, N10···N6 = 4.36, C46···N7 = 3.62, C46···N9 = 3.83, C46···N6 = 4.27, and C46···N4 = 4.34 Å (Table 2). In the preliminary result of MeCN@**2**, corresponding atomic distances were N$_{ntrile}$···NH = 3.74–4.21 Å and C$_{nitrile}$···NH = 3.76–4.15, respectively, in the mode similar to those of EtCN@**2**·EtCN. In the center of EtCN@**2**·EtCN, the methylene carbon atom, C47, of propinonitrile was 3.66 and 3.62 Å apart from least-square planes of the top and bottom benzene rings, and methyl substituent groups of the
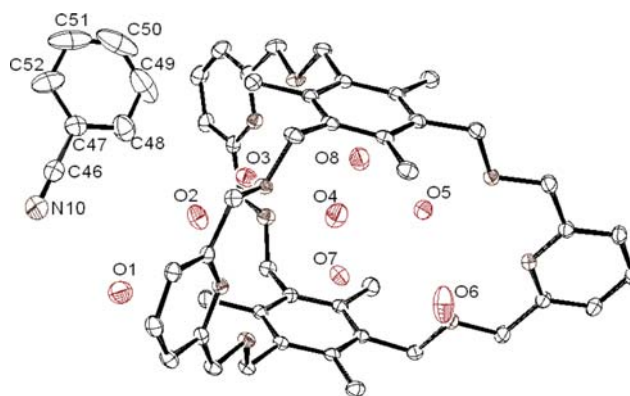
Fig. 4 ORTEP view of 8H$_2$O@**2**·PhCN drawn with the thermal ellipsoids at the 30% probability level and atomic labeling scheme. All hydrogen atoms were omitted for clarity

benzene rings were significantly close to the nitrile N10 atom (C33···N10 = 3.54 Å and C42···N10 = 3.40 Å), along the C33···N10···C42 axis.

Recrystallization of **2**·6H$_2$O in benzonitrile/*n*-hexane gave pure crystals of 8H$_2$O@**2**·PhCN. X-ray diffraction analysis of the crystal revealed that **2** captured eight water molecules having hydrogen bonding networks, with secondary amino groups of **2** (Fig. 4); O1···O2 2.81, O2···O3 2.82, O3···O4 2.78, O4···O5 2.77, O4···O7 2.76, O5···O8 2.81, O6···O7 2.77, N1···O1 3.49, N2···O1 3.47, N1···O2 3.43, N2···O2 3.12, N3···O2 3.00, N4···O3 3.04, N5···O3 3.24, N6···O3 3.03, N7···O5 3.08, N8···O5 3.29, N9···O5 3.07, N7···O6 3.07, N8···O6 3.24, N9···O6 3.59, N1···O7 2.98, N2···O7 3.36, N3···O7 3.24, N4···O8 3.09, N5···O8 3.15, and N6···O8 3.21 Å. In this crystal, the benzonitrile molecule was excluded besides the cage molecule **2** and was located near the host molecule **2**. This is because the benzonitrile molecule may be too large to be encapsulated in the cavity of **2**. The selected bond lengths and angles of 8H$_2$O@**2**·PhCN are listed in Table 2. The bond lengths and angles of the outer benzonitrile were normal; C46–N10 = 1.142(3), C47–C46 = 1.443(3) Å and C47–C46–N10 = 179.7(2)°.

These X-ray studies for MeCN@**2**·2H$_2$O, EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN clearly showed association and dissociation modes between the host molecule **2** and guest nitrile molecules in the solid state. However, the difference between interacted and non-interacted nitrile molecules was not exactly detected by the X-ray crystal structures. Therefore, we performed infrared (IR) spectroscopic measurement for these samples for characterization of the C ≡ N bond states. The IR spectral data for MeCN@**2**·2H$_2$O, EtCN@**2**·EtCN and 8H$_2$O@**2**·PhCN were given together with liquid nitrile and vapor nitrile compounds in Table 3. An IR spectrum of the crystalline product for MeCN@**2**·MeCN·2H$_2$O clearly showed that the peak assignable to the C ≡ N stretching vibration was

Table 3 The peaks assigned to the C ≡ N stretching vibration of MeCN@**2**·MeCN·2H₂O, EtCN@**2**·EtCN and 8H₂O@**2**·PhCN, and nitrile compounds [23] (cm⁻¹)

	MeCN@**2**·MeCN·2H₂O	EtCN@**2**·EtCN	8H₂O@**2**·PhCN
Solid state (KBr)	2240	2241	2226
	MeCN	EtCN	PhCN
Vapor state [23]	2266	2262	2238
Liquid state [23]	2253	2247	2228

observed at 2240 cm⁻¹, which shifted to the lower energy region by 13 cm⁻¹ than that of liquid acetonitrile (2253 cm⁻¹) [23] and by 26 cm⁻¹ than that of vapor acetonitrile (2266 cm⁻¹) [23]. IR spectral data of EtCN@**2**·EtCN also showed that the peak assignable to the C ≡ N stretching vibration at 2241 cm⁻¹ shifted to the lower energy region by 6 cm⁻¹ than that of liquid propionitrile (2247 cm⁻¹) [23] and by 21 cm⁻¹ than that of vapor propionitrile (2262 cm⁻¹) [23]. In the both cases, only one broad peak was observed regardless of the some different situations in the crystal. Whereas, IR spectral measurement of the crystalline product for 8H₂O@**2**·PhCN clearly showed that the peak assignable to the C ≡ N stretching vibration was observed at 2226 cm⁻¹, which slightly shifted to the lower energy region by 2 cm⁻¹ than that of liquid benzonitrile (2228 cm⁻¹) [23] and by 12 cm⁻¹ than that of vapor benzonitrile (2238 cm⁻¹) [23]. Taking account for these IR spectral data, we considered that the nitrile bonds of guest molecules captured in the cage **2** were affected by intermolecular multiple interaction between the nitrile compound and the cage framework in those crystal structures as identified before.

Conclusion

We synthesized a new amine-type host molecule **2**, capturing small molecules as a guest. X-ray studies of MeCN@**2**·MeCN·2H₂O, EtCN@**2**·EtCN, and 8H₂O@**2**·PhCN have revealed that acetonitrile and propionitrile molecules are captured inside the cage of **2**, whereas benzonitrile molecule is come out from the host molecule. The IR spectral measurements of these samples clearly showed that the C ≡ N stretching vibration of the captured acetnitrile and propionitrile in **2** shifted to a lower energy regions than those of their vapor states, by 21–26 cm⁻¹, which are significantly affected than that of crystalline benzonitrile divided from **2**.

References

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