Porous Coordination Polymers

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A Porous Coordination-Polymer Crystal Containing One-Dimensional Water Chains Exhibits Guest-Induced Lattice Distortion and a Dielectric Anomaly**

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Porous crystals containing guest molecules provide a unique opportunity for developing new molecular materials with functions that depend on the guest molecules and also for studying the fundamental physical properties of nanomolecular assemblies confined in confined spaces. It is clear that the storage of molecules is the most fundamental function of porous crystals arising from the porosity of the host lattice.[1,2] Other characteristic functions of porous crystals include those derived from guest-dependent physical properties, such as guest-modulated spin-crossover, and ferromagnetic (or ferrimagnetic) properties of host lattices that contain magnetic transition-metal atoms such as Fe^{2+} and Mn^{2+}.[3–6] In addition to the functions that originate from the host lattices, porous crystals can exhibit functions that are derived from guest molecules. Thus, for example, we have reported the porous crystalline compound $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$, which exhibits a dielectric anomaly associated with the "melting" (or "freezing") of the positional freedom of guest methanol and water molecules.[7] In some cases, it may even be possible to develop multifunctional systems with functions that originate from both host lattices and guest molecules. Recently, we reported the development of "multiferroic" materials that combine porous magnetic coordination-polymer crystals and polar guest molecules[8] and found that $[Mn_3(HCOO)_6](C_2H_5OH)$ exhibits ferroelectric and ferrimagnetic phase-transitions at 165 and 8.5 K, respectively. The ferrimagnetic properties of this compound are due to the Mn^{2+} ions in the host lattice and the ferroelectric properties originate from the guest ethanol molecules.[8]

Recently, Horiuchi et al. reported very interesting molecular crystals that exhibit remarkable dielectric properties. For example, they have shown that the charge-transfer complex phenazine/chloranilic acid is a new ferroelectric material that exhibits a large dielectric constant (ε_r) of up to 3000 at around room temperature.[9,10] They have also reported that a series of well-known charge-transfer complexes, namely (4,4′-dimethyltetrathiafulvalene)(QBr_nCl_{4-n}) (QBr_nCl_{4-n} = tetrahalo-*p*-benzoquinone), exhibit ferroelectric transitions near 0 K during which a quantum critical dielectric behavior is observed.[11] Although the nature of these new charge-transfer molecular dielectrics is very attractive, porous dielectric materials should possess another important and unique property, namely that the dielectric properties of porous molecular crystals containing polar guest molecules could provide useful information required to clarify the physical properties of isolated molecular assemblies confined in small spaces. In other words, the behavior of unique molecular systems, particularly isolated nanomolecular assemblies, can be investigated by taking advantage of this porous space. Herein we report the synthesis of a porous crystal $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ ($NH(CH_2COO)_2$ = iminodiacetate) that contains a large number of guest water molecules and which exhibits large dielectric anomalies at around 180 and 350 K.

It is well-known that H_2O exhibits an exceptionally high polarizability in the liquid state ($\varepsilon_r \approx 80$ at 295 K), whereas its dielectric constant decreases considerably in the crystalline state ($\varepsilon_r \approx 2.5$ at 5 K).[7] The guest molecules in a porous lattice are considered to have large positional freedom at high temperature even though they are confined to small anisotropic spaces; however their positions are fixed at low temperatures. Consequently, the dielectric properties of porous crystals that contain many guest water molecules should show a high temperature-dependency and provide important information for clarifying the thermal behavior of nanoassemblies of water molecules. $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ crystallizes in a trigonal unit cell with guest water molecules in the channels along the *c* axis.[12] La^{3+} cations and $[Cu\{NH(CH_2COO)_2\}_2]^{2-}$ anions form a honeycomb structure in the crystal, as shown in Figure 1a. These crystals were prepared according to the procedure described in the literature,[12] where it is reported that the guest water molecules are gradually lost at 50–130 °C and that the host lattice is stable up to approximately 300 °C.[12]

Thermogravimetric analysis (TGA) was performed with freshly obtained crystals maintained in a saturated water-

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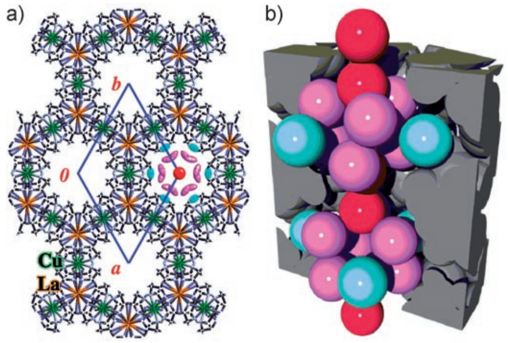

Figure 1. a) Crystal structure of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ ($n \approx 9$) at 280 K viewed along the *c* direction (channel direction). b) Schematic view of the inner region of the channel showing the arrangement of guest water molecules (at 280 K). There are three independent oxygen atoms for guest water molecules (O5 (light blue), O6 (red), O7 (pink); see also Figure 3 b).

vapor atmosphere to confirm the number of guest water molecules (n) present in the complex. The 12 % weight loss at around 340 K indicates that n is around 9.4 (Figure 2 a). Differential scanning calorimetry (DSC) measurements were conducted at 120–320 K at increasing temperatures (Figure 2 b). A baseline shift, which indicates the existence of a second-order phase transition, is observed at around 160 K[13,14] along with an endothermic peak at 260 K. The anomalous DSC behavior observed above 280 K is consistent with the TGA curve and suggests the onset of guest water molecules loss from the one-dimensional channels.

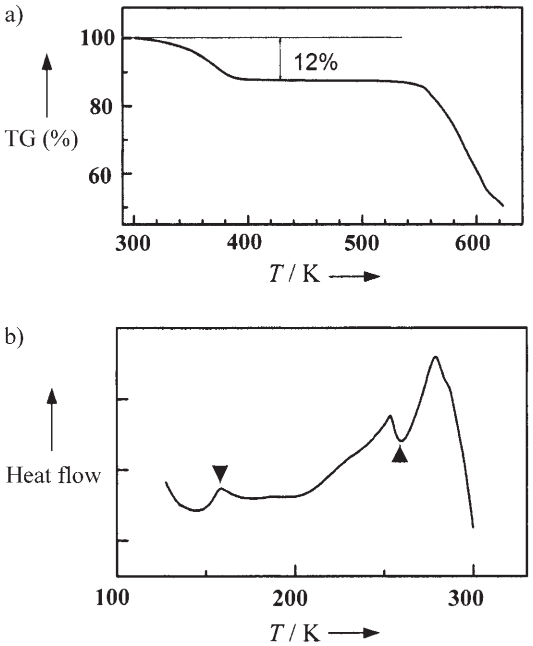

Figure 2. a) TGA curve measured up to approximately 620 K. This curve suggests that all the guest water molecules are lost in the range 300–380 K ($[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n \rightarrow [La_2Cu_3\{NH(CH_2COO)_2\}_6]$). The 12% weight loss at 300–380 K suggests that $n \approx 9.4$. b) DSC curve measured with increasing temperature. The triangles at approximately 160 and 260 K indicate the temperatures of the baseline shift and endothermic peak, respectively, which correspond well to the onset temperature of the increase in the dielectric constants for $E \parallel c$ (see Figure 4 a).

The temperature dependency of the lattice constants was examined at 120–415 K to obtain detailed information regarding the variation of the arrangement of guest water molecules with temperature (Figure 3 a); X-ray reflection data were collected at 365, 350, 280, 230, 180, and 110 K.[15] Most of the X-ray experiments were performed with the crystal sealed in a glass capillary together with very small water droplets to avoid the loss of guest water molecules from the host lattice at temperatures above room temperature. The structure was refined satisfactorily. The structure obtained at 280 K is, clearly, essentially the same as the room-temperature structure reported previously,[12,15] and at 365 K no difference Fourier peaks corresponding to guest water molecules could be found in the channel. At temperatures below 350 K, however, water molecules (oxygen atoms O5, O6, and O7; see Figure 3 b) could be located. As shown in Figure 1 b, the

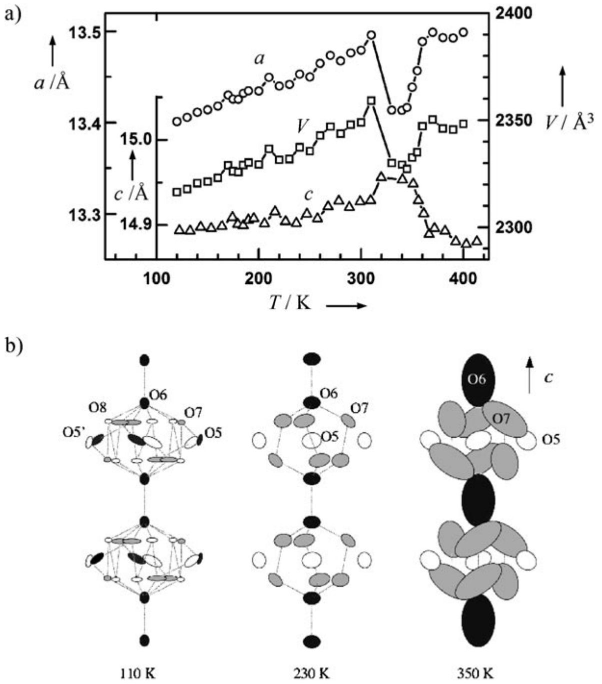

Figure 3. a) Temperature dependency of the lattice constants of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ ($n \approx 9$). b) The arrangement of guest water molecules (O5, O6, and O7) along the *c* axis at 350, 230, and 110 K. The dotted lines indicate short O···O contacts (< 2.8 Å). The representative short O···O distances are: 2.63 Å (O7···O7) at 350 K; 2.64 (O7···O7), 2.70 (O6···O7), and 2.71 Å (O6···O6) at 230 K,; 2.42 (O7···O8), 2.47 (O5···O7), 2.68 (O6···O6), and 2.65 Å (O8···O8) at 110 K. The shortest contacts between the atoms of the host lattice and the oxygen atoms of guest molecules are observed between O (host lattice) and O*m*: no contact (< 3.3 Å) at 350 K, 3.09 Å (O(host lattice)···O5) at 230 K, and 2.96 Å (O(host lattice)···O8) at 110 K. The arrangements at 180 and 280 K are almost the same as the arrangement at 230 K. At 110 K, the positions of O5 and O7 are split into two positions (white and gray ellipsoids) (O5→O5, O5′ and O7→O7, O8). Owing to the short O5···O5′ and O7···O8 distances, these positions ((O5, O5′) and (O7, O8)) cannot be occupied simultaneously. The positions of oxygen atoms at 365 K could not be determined.

diameter of the channel is not uniform along the c axis but is contracted at around $z = 0.0$ and 0.5. Most of the guest water molecules are located in the large spaces at around $z = 0.25$ and 0.75.[12] The occupancy probabilities of the oxygen atoms of the guest water molecules determined by structure refinements are as follows: 0.7 (O5), 1.0 (O6), and 0.6 (O7) at 350 K; 1.0 (O5), 1.0 (O6), and 0.7 (O7) at 280, 230, and 180 K, respectively. These results suggest that the number of guest water molecules (n) is approximately 9.2, which is in good agreement with the value (9.4) obtained from the TGA experiments.[16] At 110 K the atomic positions of O5 and O7 are split into two positions: O5→O5 (0.5), O5′ (0.5), where O5 and O5′ are crystallographically equivalent (the figure in brackets is the occupancy probability), and O7→O7 (0.7), O8 (0.7), where O7 and O8 are on the general positions. Since the O5···O5′ distance is too short for both positions to be occupied simultaneously, they are considered to be randomly occupied. A similar situation is observed for O7 and O8. Since the positions of the oxygen atoms at temperatures below 350 K were determined from X-ray data collected with the same sample used for data collection at 365 K, the unsuccessful determination of the positions of the guest water molecules at 365 K is clearly not due to the escape of guest water molecules from the channel but to the very large thermal motion in the channel, as if the molecules were in a "one-dimensional liquid state".

The temperature dependency of the lattice constants shows distinct anomalies between 315 and 360 K (Figure 3a)—the lattice constants a and V exhibit fairly sharp minima at around 340 K. As mentioned above, the positions of the guest water molecules are considered not to be fixed at temperatures above 360 K. The structure refinement at 350 K shows that the positions of the oxygen atoms of the guest water molecules begin to be fixed at this temperature despite their significantly large thermal motions (see Figure 3b). It therefore appears that the sharp decrease in the unit cell volume with decrease in temperature from 360 to 350 K is associated with the onset of "partial freezing" of the guest water molecules in the channel. Generally, it is considered that the contact between the host lattice and guest molecules is very loose, although it appears that the rigid host lattice is unexpectedly sensitive to changes in the state of the guest molecules. Furthermore, and more surprisingly, the lattice constants a and V increase very sharply at approximately 320 K. Considering that the volume of bulk water expands at the freezing point due to formation of the "ice state", this anomaly suggests the development of hydrogen bonds between the guest water molecules in the channels. As mentioned before, the structure refinements at various temperatures show that disorder in the guest water molecules remains even at temperatures below 280 K. Such a situation will be very important for the system to exhibit a large dielectric constant. If the positions of the guest molecules are completely fixed, the electric susceptibility will become very small.

The dielectric constant (ε_r) of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ was measured in the range 4.2–380 K for fresh crystals with sizes of approximately $1.0 \times 1.0 \times 0.5\ mm^3$ ($E = 1$ V, 10 kHz; Figure 4a). ε_r is small ($\varepsilon_r \approx 7$) for $E \perp c$ over the whole temperature range examined, whereas for $E \parallel c$ it exhibits a large temperature dependence. ε_r increases sharply at temperatures around 165 K and reaches a maximum ($\varepsilon_r \approx 150$) at 180 K. Since the guest-free compound $[La_2Cu_3\{NH(CH_2COO)_2\}_6]$ exhibits a very small and almost temperature-independent dielectric constant ($\varepsilon_r \approx 5$) for both $E \parallel c$ and $E \perp c$, it is clear that the large dielectric constant for $E \parallel c$ must be due to the guest water molecules. In contrast to bulk water, however, the ε_r value of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ is highly anisotropic, although this characteristic dielectric behavior was observed only for $E \parallel c$. Furthermore, the maximum value of ε_r ($E \parallel c$) of around 150 is significantly higher than that of bulk water ($\varepsilon_r(H_2O) \approx 90$ at 273 K).[7] The dielectric behavior for $E \parallel c$ at around 180 K resembles that of bulk water, which exhibits a sharp drop of ε_r at the freezing point.[7] The sharp decrease in ε_r in the range 160–180 K and the very small value of ε_r below 160 K indicate that the freezing of the positional freedom of guest water molecules occurs at approximately 160 K, although only the average structure could be determined from the X-ray structure analysis. It appears that the anomaly in the DSC curve at around 160 K corresponds well to the onset of this increase in ε_r. In contrast to the conspicuous lattice distortion at around 340 K, the lattice constants show no remarkable change at around 160 K.

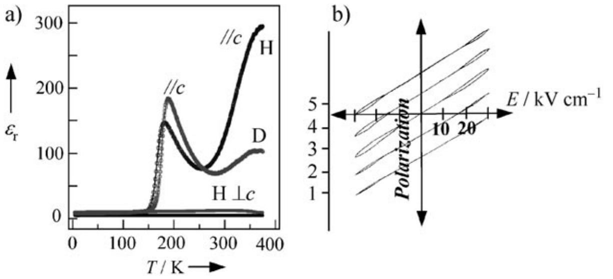

Figure 4. a) Dielectric constants (ε_r) of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ for $E \parallel c$ (black) and $E \perp c$ (gray). The horizontal lines indicate ε_r of the guest-free crystal $[La_2Cu_3\{NH(CH_2COO)_2\}_6]$ ($E \parallel c$ and $E \perp c$). The gray curve (D) indicates ε_r of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](D_2O)_n$ for $E \parallel c$. H and D represent the H_2O and D_2O crystals, respectively. b) Hysteresis loop of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ observed at around 350 K. 1: 295 K, 2: 309 K, 3: 352 K, 4: 369 K, 5: 373 K.

At temperatures above 180 K the ε_r of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ ($E \parallel c$) decreases in a fairly rapid manner with an increase in temperature and reaches a minimum at around 250 K ($\varepsilon_r \approx 75$ at 250 K). The ε_r value then increases in a fairly sharp manner with increasing temperature and reaches as high as 300 at around 370 K, which is more than three times the maximum ε_r value of water (ca. 90 at approximately 273 K). The anomaly in the DSC curve at around 260 K appears to correspond to the onset of the increase in dielectric constants. The increase in ε_r tends to be sluggish at temperatures above 340 K, which is probably related to loss of the guest H_2O molecules, as suggested by the TGA and DSC curves (Figure 2). The reliability of the unexpectedly large ε_r value of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ was verified by confirming that the expected dielectric constants were obtained from dielectric measurements using the same instrument with an artificial circuit constructed from a condenser (*C*) and resistance (*R*) with *C*- and *R*-values approximately equal to those of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ at around 350 K.

It is quite surprising that the characteristic antiferroelectric hysteresis loop is observed at around 350 K even though the guest H_2O molecules begin to be lost fairly rapidly at around this temperature (Figure 4b). Although the lack of accurate data prevented the transition temperature from being determined accurately, these results show that the large enhancement of the ε_r value of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ (for $E \parallel c$) above 300 K is due to an antiferroelectric ordering of the guest water molecules. The dielectric ordering suggests a correlation between the H_2O arrangements of neighboring channels. As mentioned before, the characteristic expansion of the host lattice is observed at temperatures below 340 K along the direction perpendicular to *c*, which suggests that the contacts between the host lattice and the guest molecules become important below the "liquid/solid transition" temperature of the guest water molecules. It can be imagined that the guest water molecules undergo a transition between an "antiferroelectric solid state" and a "one-dimensional liquid state" at around 350 K because of the development of host/guest contacts. On the other hand, it should also be noted that a faint hysteresis loop is observed up to approximately 370 K. The short-range order therefore probably survives up to a fairly high temperature owing to the one-dimensionality of the water system.

The dielectric properties of a crystal containing D_2O instead of H_2O were also examined. Similar to $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$, the ε_r value of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](D_2O)_n$ shows a sharp peak at around 190 K, which is approximately 10 K higher than the peak temperature of the H_2O crystal (Figure 4a). This "deuteration effect" is also observed at temperatures above 200 K. As shown in Figure 4a, the ε_r value of the D_2O crystal reaches a minimum at 280 K, which is approximately 25 K higher than the corresponding temperature for the H_2O crystal. The ε_r value of the D_2O crystal begins to increase above 280 K, although all D_2O molecules are lost before the value of ε_r becomes sufficiently large. Consequently, large enhancements in the ε_r value and the hysteresis loop similar to those observed for $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ are not observed for $[La_2Cu_3\{NH(CH_2COO)_2\}_6](D_2O)_n$. Although the strong tendency of the water molecules to escape above 340 K conceals the presence of the dielectric transition of the D_2O crystal, these results suggest that the antiferroelectric transition temperature is enhanced by the deuteration of water and that the hydrogen bond appears to play an essential role in the "liquid/solid transition" of the guest water molecules, as expected.

In conclusion, the porous molecular crystal $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ ($n \approx 9$) exhibits characteristic dielectric anomalies at around 180 and 350 K. The dielectric constant reaches a maximum ($\varepsilon_r \approx 150$) at 180 K and then drops sharply to around 7 below 160 K for the electric field parallel to the channel direction ($E \parallel c$). The value of ε_r for $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ increases significantly at temperatures above 300 K. The hysteresis loop indicates an antiferroelectric transition at around 350 K. The dielectric measurements, X-ray structure refinements at various temperatures, and the temperature dependency of the lattice constants suggest that the guest water molecules confined in the channels of $[La_2Cu_3\{NH(CH_2COO)_2\}_6]$ undergo a transition between a "one-dimensional liquid state" and an "antiferroelectric solid state" at around 350 K, where the host lattice is strongly distorted. The dielectric measurements with the deuterated analogue $[La_2Cu_3\{NH(CH_2COO)_2\}_6](D_2O)_n$ show a considerable isotope effect. Hydrogen bonding plays an essential role in the dielectric properties of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$.

Experimental Section

Crystals of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](H_2O)_n$ were prepared by treating $LaCl_3{\cdot}9\,H_2O$ with a mixture of iminodiacetic acid and $Cu(NO_3)_2{\cdot}3\,H_2O$ in an aqueous solution according to the method reported previously.[12] The guest water molecules were removed by keeping the crystal at approximately 50 °C under vacuum. Crystals of $[La_2Cu_3\{NH(CH_2COO)_2\}_6](D_2O)_n$ were obtained by storing guest-free $[La_2Cu_3\{NH(CH_2COO)_2\}_6]$ under a saturated D_2O atmosphere for two weeks. TGA data were obtained with a Rigaku TG8120 up to 623 K. DSC measurements were performed in the temperature range 120–320 K with a Rigaku DSC8230. The X-ray diffraction experiments were performed with a Rigaku CCD Mercury diffractometer at 110–415 K. The temperature-dependency of the dielectric constants was measured in the temperature range 4.2–380 K with an LCR meter (Precision Component Analyser 6440B from Wayne Kerr Electronics). The single crystals were cut into rectangular parallelepipeds. The approximate dimensions of a typical crystal were $1.0 \times 1.0 \times 0.5\ mm^3$. Gold conduction paste painted on the crystal surfaces was used as the electrodes. A 10-kHz electric field of 1 V was applied. The accuracy of the obtained dielectric constant (absolute value) was not sufficiently high due to the difficulties encountered in shaping the crystals, athough the temperature dependency could be determined in a fairly precise manner.

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[15] The structural data obtained were almost the same as those in the original report (ref. [12]). The crystal belongs to the trigonal system with space group $P\bar{3}c1$ (no. 165). The lattice constants are: $a = 13.4386(19)$, $c = 14.888(3)$ Å, $V = 2328.49$ Å^3, and $R = 0.0218$ at 365 K; $a = 13.3819(19)$, $c = 14.933(3)$ Å, $V = 2315.87$ Å^3, and $R = 0.0306$ at 350 K; $a = 13.5039(19)$, $c = 14.897(3)$ Å, $V = 252.60$ Å^3, and $R = 0.0269$ at 280 K; $a = 13.5156(19)$, $c = 14.872(3)$ Å, $V = 2352.72$ Å^3, and $R = 0.0309$ at 230 K; $a = 13.5045(19)$, $c = 14.836(3)$ Å, $V = 2343.17$ Å^3, and $R = 0.0299$ at 180 K; $a = 13.5136(19)$, $c = 14.794(3)$ Å, $V = 2339.69$ Å^3, and $R = 0.0339$ at 110 K. CCDC 669701, 669702, 669703, 669704, 669705 and 669706 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] Based on X-ray structure analysis, the number of guest water molecules (n) was calculated to be 9.2 ($n = (1.0\times3) + (1.0\times2) + (0.7\times6)$) on the basis of the refined occupancy factors (1.0 (O5), 1.0 (O6), and 0.7 (O7)) at 280, 230, and 180 K. This value of n is in good agreement with that estimated from the TGA experiment ($n = 9.4$).